

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent
appln. of : Ming Liang Shiao, et al.

Appln. No: 10/679,898

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For: **COLORED ROOFING GRANULES WITH
INCREASED SOLAR HEAT
REFLECTANCE, SOLAR HEAT-
REFLECTIVE SHINGLES, AND
PROCESS FOR PRODUCING SAME**

Group Art
Unit: 1773

Examiner: Leszek B. Kiliman

Confirmation No.: 3803

Docket No: 077-03

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPEAL BRIEF

Sir:

This corrected appeal brief is being submitted electronically on January 4, 2007 in support of the Notice of Appeal filed July 27, 2006. An appeal brief was filed in this matter on October 27, 2006. A Notification of Non-Compliant Appeal Brief was mailed December 7, 2006, noting that the summary of claimed subject matter did not identify and map independent claim 32 to the specification by page and line number. This corrected brief includes the required identification and mapping regarding claim 32 on page 5.

I. Real Party in Interest

The real party in interest is CertainTeed Corporation, a Delaware corporation.

II. Related Appeals and Interferences

There are no related appeals or interferences.

III. Status of the Claims

Claims 1-32 have been rejected.

Claims 33-35 have been withdrawn as drawn to a non-elected invention.

The claims on appeal are claims 1-32.

IV. Status of Amendments

There were no amendments filed subsequent to final rejection.

V. Summary of the Claimed Subject Matter

The easiest way to reduce summer air conditioning expenses is to paint your roof white. Unfortunately, there are major drawbacks to this approach: For example, white roofs can become dirty very quickly, so the roof must be repainted frequently. More importantly, most people prefer a traditional roof color, such as a dark blue, grey, green, brown or red. The present invention is directed to those people, and provides roofing granules and products that have desirable deep-tone colors as well as increased solar heat reflectance.

In particular, as embodied in independent claim 1, the presently claimed invention relates to colored infrared roofing granules (Fig. 1, 10) with size passing #8 mesh and retaining on #70 mesh (page 9, lines 21-23). The roofing granules (10) are coated with a cured coating composition (14) comprising a coating binder (16) and at least one colored, infrared pigment (18; page 9, line 31 - page 10, line 9; page 11, line 11 - page 10, line 21).

As embodied in independent claim 6, the presently claimed invention relates to colored, infrared-reflective roofing granules (Fig. 2, 30) comprising base particles (12)

with size passing #8 mesh and retaining on #70 mesh (page 9, lines 21-23). The roofing granules (30) are coated with a cured coating composition (34) comprising a coating binder (36) and at least one colored, infrared-reflective pigment (38; page 9, line 31 - page 10, line 9; page 11, lines 11-18). Further, the base particles (12) comprise mineral particles (32) coated with a cured base coating composition (34). The base coating composition (34) includes a base particle binder (36), and at least one reflective white pigment (38; page 12, line 22 - page 13, line 27, and Fig. 2).

As embodied in independent claim 8, the presently claimed invention relates to colored, infrared-reflective roofing granules (Fig. 3, 50) comprising base particles (52) comprising inert mineral particles (54) coated with a cured first coating composition (56) including a base particle binder (58) and at least one reflective white pigment (60). The base particles (52) are coated with a cured second coating composition (62) including a coatings binder (54), and at least one colorant (66) selected from the group consisting of uv-stabilized dyes and granule coloring pigments (page 13, line 28 - page 15, line 12, and Fig. 3).

As embodied in independent claim 13, the presently claimed invention relates to colored infrared-reflective roofing granules (Fig. 4, 70) comprising inert mineral particles (74) coated with a cured first coating composition (76) including a base particle binder (78) and at least one colorant (80) selected from the group consisting of uv-stabilized dyes and granule coloring pigments to form base particles (72). The base particles (72) are coated with a cured second coating composition (84) including a coating binder (86) and at least one infrared-reflective functional pigment (88) selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina (page 15, line 13 - page 16, line 18, and Fig. 4).

As embodied in independent claim 17, the presently claimed invention relates to a bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material (page 24, lines 11-26) and colored, infrared-reflective roofing granules (Fig. 1, 10) comprising base particles with size passing #8 mesh and retaining on #70 mesh (page 9, lines 21-23) coated with a cured coating composition (14) comprising a coating binder (16) and at least one colored, infrared-reflective pigment (18).

As embodied in independent claim 23, the presently claimed invention relates to a bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material (page 24, lines 11-26) and colored infrared-reflective roofing granules (Fig. 3, 50) comprising base particles (52) comprising inert mineral particles (54) with size passing #8 mesh and retaining on #70 mesh (page 9, lines 21-23) coated with a cured first coating composition (56) including a base particle binder (58) and at least one reflective white pigment (60). The base particles (52) are coated with a cured second coating composition (62) including a coating binder (54), and at least colorant (56) selected from the group consisting of uv-stabilized dyes and granule coloring pigments.

As embodied in independent claim 28, the presently claimed invention relates to a bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material (page 24, lines 11-26) and colored infrared-reflective roofing granules (Fig. 4, 70) comprising inert mineral particles (74) with size passing #8 mesh and retaining on #70 mesh (page 9, lines 21-23) coated with a cured first coating composition (76) including a base particle binder (78) and at least one colorant (80) selected from the group consisting of uv-stabilized dyes and granule coloring pigments to form base particles (72). The base particles (72) are themselves coated with a cured second coating composition (84) including a coating binder (86) and at least one

infrared-reflective functional pigment (88) selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, and mirrorized silica pigments based upon metal-doped silica.

As embodied in independent claim 32, the presently claimed invention relates to a mineral surfaced asphalt shingle having $L^* < 60$ and solar reflectance $> 25\%$ (page 4, line 33-page 5, line 6; page 23, line 30 - page 31, line 1; page 34, claim 32).

VI. Grounds of Rejection To Be Reviewed On Appeal

A. Claims 1, 4-8, 11-12, 17, 20-23, 26-28 and 31 were rejected as anticipated under 35 U.S.C. § 102(e) by U.S. Patent 6,521,038 ("Yanagimoto '038").

B. Claims 2-3, 9-10, 13-16, 18-19, 24-25, 29-30, and 32 were rejected as obvious under 35 U.S.C. § 103(a) by Yanagimoto.

VII. Argument

The sole reference cited by the Examiner, Yanagimoto '038 discloses an improvement over a method disclosed in a Japanese patent publication for reducing the solar heat-induced temperature rise in interior rooms of a building. The Japanese patent publication apparently disclosed coating the outer wall of the building with a white paint to form an undercoat and then covering that undercoat with an infrared reflecting paint to prevent absorption of direct sunlight. Instead of using separate coats containing white pigment and infrared reflecting pigment, Yanagimoto '038 discloses a composite pigment formed by coating white pigment with infrared-reflecting pigment, and coating compositions including that composite pigment. The present invention takes a different approach: No composite pigment is used. Instead of painting an exterior surface with a coating composition, individual roofing granules are coated with coating compositions containing infrared-reflecting pigments. The granules themselves are then used in manufacturing bituminous roofing products. The present invention provides coated

infrared-reflective granules and roofing products that look like the traditional roofing materials valued by consumers, but which also help reduce energy consumption. The cited art does not, and neither anticipates nor makes obvious this invention.

A. Claims 1, 4 and 5 Are Not Anticipated By Yanagimoto '038

In making his final rejection, the Examiner stated that Yanagimoto '038 discloses colored infrared-reflecting roofing granules comprising base particles coated with a cured coating composition comprising a binder and infrared reflecting pigment. The Examiner's characterization of Yanagimoto '038 is not correct. Yanagimoto '038 has nothing to do with roofing granules or roofing products incorporating roofing granules. Instead, Yanagimoto '038 discloses near-infrared reflecting *composite pigments*.

Yanagimoto '038 Example 2, cited by the Examiner, is illustrative. A dispersion of a black, near-infrared reflecting azo compound is mixed with titanium oxide pigment to coat the titanium dioxide with a layer of the azo compound, and dried to form the composite pigment.

The near-infrared reflective composite pigments can be used to prepare near-infrared reflecting coating agents, such as paints and inks, colored by the composite pigments. The near-infrared coating agents can be used to prepare near-infrared reflecting materials comprising a base material coated on a surface thereof with the near-infrared coating agent. Thus, the composite pigment of Example 2 can be used to prepare an alkyd varnish (Examples 13-16) or a offset lithographic ink (Example 18). The resulting varnish and ink can be used as coating materials for metal plates or paper.

The Examiner cites to the abstract, column 1, lines 20-40, column 2 lines 1-22, lines 35-42, lines 54-67, column 4, lines 60-67, column 5, lines 1-31, lines 50-67, Example 2, and the claims.

Yanagimoto '038 does not disclose each and every limitation of the presently claimed invention, and thus does not anticipate the presently claimed invention.

Yanagimoto '038 relates to near-infrared reflecting composite pigments. These composite pigments are formed by mixing a near-infrared reflecting colorant dispersion with a white pigment powder or white pigment dispersion, and then drying the dispersion. The near-infrared colorant is preferably dispersed as an aqueous dispersion using hydrophilic high molecular weight dispersant. The dispersant is preferably subsequently rendered insoluble so that the white pigment powder is coated with the near-infrared colorant. The resulting composite pigment can be used in formulating inks and coatings. The composite pigment "obviates a white undercoat or the like" which had previously been required to achieve near-infrared reflectivity.

In contrast, as claimed in amended independent claim 1, the present invention is directed to colored infrared-reflective *roofing granules* comprising inert base particles with size passing #8 mesh and retaining on #70 mesh coated with a cured coating composition comprising a coating binder and at least one colored, infrared-reflective pigment. The inert base granules are *much larger* than the white pigment powder employed by Yanagimoto '038.

Yanagimoto '038 does not disclose expressly the particle sizes of the white pigments used. However, materials that can be used as pigments are inherently much smaller than the claimed roofing granules. Many common coatings problems are associated with poorly dispersed pigment - that is, pigment that is too big. Roofing granules, such as those presently claimed, are orders of magnitude larger than typical coating pigments, simply could not be employed as pigments.

Yanagimoto '038 employs "white pigments [that] are all available on the market . . ." (col. 4. lines 51-52) – commercially available white pigments. However, it is well known in the art that materials useful as pigments should have the largest practical

surface area and, equivalently, the smallest practical particle size, in order to be useful. For example, in the case of organic pigments, “(f)or practical use, organic pigments having approximate particle sizes of from 0.01 to 0.1 μm for transparent forms and from 0.1 to 10 μm for opacifying forms have proved most suitable.” United States Patent 6,423,132, col. 1, lines 11-15 (reproduced in the Evidence Appendix). Similarly, “[i]norganic pigments are normally produced for and used in the paints, plastics, or elastomer industries, and are in the form of a finely divided powder.” United States Patent 6,908,675, col. 1, lines 49-51 (reproduced in the Evidence Appendix). There is a substantial art concerning granulating pigment powders to make them easier to use. For example, U.S. Patent 6,908,675 relates to agglomerating “materials less than about one micron in average diameter, and . . . preferably . . . pigments and fillers, having average particle sizes of about 0.01 to about 10 microns” (col. 4, lines 19-20). Thus, commercially available white pigment “powder” means particles with average particle sizes less than about 10 microns.

In contrast, as amended claim 1 requires “base particles” which will be retained on a #70 mesh screen, so that the average particle size must be greater than about 200 micrometers¹, an average size at least twenty times greater than Yanagimoto ‘038’s white “pigment” and an average particle volume at least about eight thousand times greater.

Claim 1 also requires “a coating binder.” This limitation is not satisfied by Yanagimoto ‘038’s disclosure of a “dispersant.” At most, when a high molecular weight ionic dispersant is used, and rendered water-insoluble by addition of multivalent ions,

¹ Applicants include for the Board’s reference a powder size conversion table made available by Chemalloy, at <http://www.chemalloy.com/psizes1.htm>, reproduced in the Evidence Appendix as Exhibit A.

the “binding force between the white pigment and the near-infrared non-absorbing colorant can be enhanced.” (col. 7, lines 10-13). There is no disclosure in Yanagimoto '038 that the pigment dispersant functions as a coating binder.

Because Yanagimoto '038 fails to disclose at least two limitations of the present invention as claimed by amended claim 1, claim 1 is not anticipated thereby.

With respect to claim 4, this claim depends from independent claim 1 and therefore includes all the limitations of claim 1, and for this reason alone cannot be anticipated by Yanagimoto '038. In addition, however, claim 4 requires that the coating composition further comprise at least one infrared-reflective functional pigment selected from a specific Markush group. However, Yanagimoto '038 does not disclose the use of a second infrared-reflective functional pigment. At most, Yanagimoto '038 discloses a composite pigment including a near-infrared non-absorbing colorant and a white inorganic pigment. However, if the white pigment is identified with the second infrared-reflective functional pigment required by claim 4, then Yanagimoto '038 fails to disclose the base particles required by claim 1 from which claim 4 depends. Because Yanagimoto '038 does not disclose all the limitations of claim 4, claim 4 is not anticipated thereby.

Claim 5 depends from independent claim 1. Yanagimoto '038 does not disclose all the limitations of claim 1. Therefore, claim 5 is not anticipated thereby.

In sum, Yanagimoto '038 does not expressly disclose nor inherently possess all the limitations of independent claim 1 and dependent claims 4 and 5. Consequently, claims 1, 4 and 5 are not anticipated by Yanagimoto '038, and the Examiner's rejection of claims 1, 4 and 5 over Yanagimoto '038 should be reversed.

B. Claims 6 and 7 Are Not Anticipated By Yanagimoto '038

Claim 6 includes the limitations of claim 1, and is therefore not anticipated by Yanagimoto '038 for the reasons provided above. Pigments are inherently too small to meet the express size limitation of claim 6. Claim 6 requires base particles, reflective white pigment, infrared-reflective pigment, as well as base particle binder. Yanagimoto '038's composite pigments are simply white reflective pigment coated with or agglomerated with infrared-reflective pigment - there is no binder and no base particle.

Thus, claim 6 includes further limitations not disclosed by Yanagimoto '038. In claim 6 the base particles are not simply inert mineral particles, but rather mineral particles that are coated with a cured base coating composition including a base particle binder and at least one reflective white pigment. Yanagimoto '038, in contrast, emphasizes that the composite pigment disclosed therein as useful for avoiding having to apply an underlying reflective layer on a substrate, and distinguishes the invention disclosed therein from prior art in which a near-infrared reflective pigment-containing coating material was applied over a coating including a reflective white pigment (col. 2, line 64 – col. 3, line 4). Because Yanagimoto '038 does not disclose all the limitations of amended claim 6, amended claim 6 is not anticipated thereby.

Claim 7 depends from independent claim 6. Yanagimoto '038 does not disclose all the limitations of claim 6. Therefore, claim 7 is not anticipated thereby.

Thus, Yanagimoto '038 does not expressly disclose nor inherently possess all the limitations of independent claim 6 and dependent claim 7. Claims 6 and 7 are not anticipated by Yanagimoto '038, and the Examiner's rejection of claims 6 and 7 over Yanagimoto '038 should be reversed by the Board.

C. Claims 8, 11 and 12 Are Not Anticipated By Yanagimoto '038

Claim 8 is another independent claim that requires two coatings on inert mineral particles.

The first coating includes a base particle binder and at least one reflective white pigment. The second coating includes a coating binder and at least one colorant.

Yanagimoto '038 discloses the coating compositions including the composite pigments and articles coated with a coating composition, a paint or ink, containing the composite pigments. However, Yanagimoto '038 avoids the use of an underlying white reflective coating layer, and therefore cannot anticipate claim 8.

Claims 11 and 12 depend from claim 8 and add further limitations. Because Yanagimoto '038 does not meet the limitations of claim 8, it cannot anticipate those claims that depend from claim 8 and add further limitations.

Thus, Yanagimoto '038 does not expressly disclose nor inherently possess all the limitations of independent claim 8 and dependent claims 11 and 12. Consequently, claims 8, 11 and 12 are not anticipated by Yanagimoto '038, and the Examiner's rejection of claims 8, 11 and 12 over Yanagimoto '038 should be reversed by the Board.

D. Claims 17 and 20-22 Are Not Anticipated By Yanagimoto '038

Claim 17 is an amended independent claim to a bituminous roofing material including roofing granules of a specific size coated with a cured coating composition including both a binder and at least one colored, infrared-reflective pigment.

Yanagimoto '038 does not disclose bituminous roofing material of any type, let alone one including roofing granules of a specific size coated with a specific coating composition. Because Yanagimoto '038 fails to disclose all the requirements of amended claim 17, amended claim 17 is not anticipated thereby.

Yanagimoto '038 discloses the preparation of a coating material incorporating the infrared-reflective composite pigment, and suggests the application of the coating material to sundry base materials, including metallic base materials such as aluminum sheets and plates, and iron sheets and plates, plastics such as acrylic resins and polycarbonates, wood, glass and ceramics (col. 7, lines 52-61), and the corresponding ink to various base materials, including paper, chemical fiber mixed paper, synthetic paper, non-woven fabric, woven fabric, plastic films, plastic sheets, plastics, metals, wood, glass and ceramics (col. 8, lines 5-10).

Claims 20-22 depend directly or indirectly from claim 17 and add further limitations. However, because Yanagimoto '038 does not meet the limitations of claim 17, it cannot anticipate those claims that depend from claim 17 and add further limitations.

Yanagimoto '038 does not expressly disclose nor inherently possess all the limitations of independent claim 17 and dependent claims 20-22. Claims 17 and 20-22 are not anticipated by Yanagimoto '038, and the Examiner's rejection of claims 17 and 20-22 over Yanagimoto '038 should be reversed.

E. Claims 23, 26 and 27 Are Not Anticipated By Yanagimoto '038

Independent claim 23 is directed to a bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material and colored infrared-reflective roofing granules formed from base particles of a specific size. As noted above, Yanagimoto '038 fails to disclose bituminous roofing products of any type. Since Yanagimoto '038 does not disclose all the requirements of amended claim 23, amended claim 23 is not anticipated thereby.

Claims 26 and 27 depend from independent claim 23 and add further limitations. Because Yanagimoto '038 does not meet the limitations of claim 23, it cannot anticipate

those claims that depend from claim 23 and add further limitations, and in particular, claims 26 and 27.

The rejection of claims 23, 26 and 27 as anticipated by Yanagimoto '038 should be reversed by the Board.

F. Claims 28 and 31 Are Not Anticipated By Yanagimoto '038

Independent claim 28 is also directed to a bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material and colored infrared-reflective roofing granules formed from base particles of a specific size.

Yanagimoto '038 does not disclose bituminous roofing products of any type.

Yanagimoto '038 does not disclose all the requirements of amended claim 28.

Therefore, amended claim 28 cannot be and is not anticipated thereby.

Claim 31 depends from independent claim 28 and adds further limitations.

Because Yanagimoto '038 does not meet the limitations of claim 28, it cannot anticipate those claims that depend from claim 28 and add further limitations, including claim 31.

The rejection of claims 28 and 31 as anticipated by Yanagimoto '038 should be reversed by the Board.

Further, Yanagimoto '038 render obvious any of claims 1, 4-8, 11-12, 17, 20-23, 26-28 or 31 to one of ordinary skill in the art.

Yanagimoto '038 is concerned with the problem of heat buildup when the outer walls or roof of a building or other structure are coated with a dark-colored paint, apparently a common practice in Japan, in order to make stains on the roof or walls hardly noticeable (col. 1, lines 20-31). Yanagimoto '038 teaches one of ordinary skill in the art faced with the problem of lowering the heat absorption of dark-colored roofs a very straightforward solution – paint the roof with a coating including Yanagimoto 038's composite pigment. This teaches away from the solution disclosed by applicants,

namely coating roofing granules with a coating composition including at least one colored, infrared reflective pigment, and then preparing bituminous roofing products including such granules.

G. Claims 2-3, 9-10, 13-16, 18-19, 24-25, 29-30 and 32
 Are Not Obvious in View of Yanagimoto '038

In his final rejection, the Examiner states that Yanagimoto '038 teaches colored infrared-reflective roofing granules comprising base particles coated with a cured coating composition comprising a coating binder and at least one infrared-reflective pigment. The Examiner admitted that Yanagimoto '038 does not specifically teach L value, infrared reflectance or a second coating for particles. The Examiner further stated that, however, the prior art reference teaches that it is well known in the art that reflection and absorption of the particles should be optimized, referencing column 1, lines 20-40. The Examiner concluded that it would have been obvious to one having ordinary skill in the art at the time of the invention to adjust L value and infrared reflectance of particles, since such would improve heat reflection properties of the roofing material. The Examiner further concludes that it would be obvious to one having ordinary skill in the art to add additional coatings to particles, since such would magnify the effects of light and heat reflection of such particles.

The Examiner's reasoning is sound, and applicants agree with the Examiner that one of ordinary skill in the art would do exactly as the Examiner has suggested: namely, optimize the reflection and adsorption of the particles by adjusting the L value and the infrared reflective properties of the particles, since this would improve the heat reflection properties of the roof. This is easily done by painting the roof white with paint heavily laden with titanium dioxide. The only residual color would be that contributed by the paint binder resin. However, one of ordinary skill in the art following the Examiner's exhortation to optimize L value and reflectivity would not arrive at the presently claimed

invention, and Yanagimoto '038 does not establish a *prima facie* case of obviousness in respect of the presently claimed invention.

As noted above, Yanagimoto '038 is concerned with the problem of heat buildup when the outer walls or roof of a building or other structure are coated with a dark-colored paint. Yanagimoto '038 expressly teaches one of ordinary skill in the art faced with the problem of lowering the heat absorption of dark-colored roofs to paint the roof with a coating including Yanagimoto 038's composite pigment. This would teach one of ordinary skill in the art away from the solution disclosed by applicants, namely coating roofing granules with a coating composition including at least one colored, infrared-reflective pigment, and using such granules in manufacturing bituminous roofing products.

In Yanagimoto 038's composite pigments, the underlying white base pigment should be covered over with the colored pigment. If the colored pigment concentration in the dispersion is too low, "the coating of the white pigment with the colorant becomes insufficient" (col. 6, lines 25-28). In contrast, in those embodiments of the presently claimed invention employing white pigments such as titanium dioxide, the titanium dioxide can be provided in an underlying or base layer. Yanagimoto '038 teaches away from providing white pigment in a separate layer. Indeed, one of Yanagimoto '038's asserted advantages is that the use of the composite pigment obviates the need to provide an underlying reflective layer including a white pigment. One of ordinary skill in the art would not employ an underlying base layer including a white pigment based on the disclosure of Yanagimoto '038. Yanagimoto '038 expressly teaches that including such a layer is disadvantageous because when repairs are to be made, the underlying white undercoat has to be repaired also (col. 1, lines 51-55).

The Examiner characterizes Yanagimoto '038 as disclosing roofing granules. This is incorrect. Yanagimoto '038 discloses composite pigments for paints that

presumably may be used for coating roofs. However, “roofing granules” is a term of art denoting particles having average dimensions about two orders of magnitude greater than those of “pigments.”

The Examiner contended that Yanagimoto '038 teaches that it is well known in the art that reflection and absorption of particles should be optimized, citing col. 1, lines 20-40. However, Yanagimoto '038 has nothing to say about optimizing the properties of particles. Instead, the portion of the disclosure to which the Examiner makes reference relates to painting roofs and the like with dark colored paints. Yanagimoto '038 discloses that the dark colored paints include pigments that absorb solar heat, while solar-reflective paints include reflective white pigments which yield white or light-colored paints. Yanagimoto '038 notes that there is an unmet demand for dark-colored, solar reflecting paints. One of ordinary skill in the art who attempted to “optimize” the absorbance and reflection properties of such paints would not arrive at applicants' invention. Instead, she would arrive at a not-so-dark colored paint that did not reflect solar heat as well as a paint based on a white pigment.

The Examiner concluded that it would have been obvious to one having ordinary skill in the art at the time of the invention to adjust the L value and infrared reflectance of particles, since such would improve heat reflection properties of the roofing material. This may be true, but this would not provide the present invention. Adjusting the L value to improve the heat reflectance of the particles is easy to do, by simultaneously maximize the L value and solar reflectance by using a white pigment. However, applicants' claims 2-3, 9-10, 14-16, 18-19, 24-25, 29-30, and 32² all require L* less than

² The Examiner has also rejected claim 13 on this basis, but claim 13 does not include a limitation as to L* or reflectance. This rejection is not understood as applicable to claim 13, and the rejection of claim 13 should be reversed for this reason also.

60 or 55, depending on the specific claim. Optimizing L^* to maximize solar reflectivity would give an L^* substantially greater than 60. This may be obvious, but it is not what the applicants have done or are claiming.

Applicants advantageously provide dark colored roofing granules with improved solar heat reflectivity. As the experimental data provided in the specification show, the inventors have been able to substantially match the color of dark colored roofing granules while significantly improving the solar reflectance by the present invention. For example, in Example 2, roofing granules having a deep, reddish gold appearance ($L^*=44.10$, $a^*=20.79$, $b^*=18.59$) were prepared. These granules had a 9 % more reflectance than granules of the same color colored with conventional inorganic pigments. Similarly, in Example 5, brown ($L^*=32.77$, $a^*=5.05$, $b^*=5.66$) roofing granules having about a 50 percent increase in solar reflectivity were prepared, compared with similarly colored granules prepared using conventional colored pigments. Further, in Example 7, off-white roofing granules having about a 60 percent increase in reflectivity were prepared according to the present invention compared with similarly colored roofing granules prepared using conventional inorganic colorants.

The present invention has great practical significance: This means that consumers can install conventional-looking roofs made up of shingles with traditional colors – and yet gain substantial energy savings. There is no need to use soon-to-get-dirty white shingles, or cover the roof with white roof coatings, just to realize energy savings. The present invention thus represents a significant advance over the composite pigment-colored paints disclosed by the cited reference.

Thus, there is nothing that discloses or would suggest the presently claimed process to one of ordinary skill in the art. The Examiner's rejection of claims 2-3, 9-10, 13-16, 18-19, 24-25, 29-30 and 32 should be reversed by the Board for these reasons.

VIII. Conclusion

The Examiner's rejection of claims 1, 4-8, 11-12, 17, 20-23, 26-28 and 31 for anticipation by Yanagimoto '038 should be reversed by the Board because the cited reference does not expressly or inherently disclose all the limitations of the invention as claimed.

Similarly, the Examiner's rejection of claims 2-3, 9-10, 13-16, 18-19, 24-25, 29-30 and 32 as obvious over Yanagimoto '038 should be reversed by the Board because even were the Examiner's reasoning correct, it is based on a misunderstanding of the cited reference's disclosure, and consequently does not make a *prima facie* case of obviousness.

Respectfully submitted,

January 4, 2007

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CLAIMS APPENDIX

CLAIMS ON APPEAL:

Claim 1. Colored infrared-reflective roofing granules comprising inert base particles with size passing #8 mesh and retaining on #70 mesh coated with a cured coating composition comprising a coating binder and at least one colored, infrared-reflective pigment.

Claim 2. Colored infrared-reflective roofing granules according to claim 1, the colored infrared-reflective roofing granules having an L* value of less than 55.

Claim 3. Colored infrared-reflective roofing granules according to claim 1 the colored infrared-reflective roofing granules having an infrared reflectance of at least 25%.

Claim 4. Colored infrared-reflective roofing granules according to claim 1 wherein the coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 5. Colored infrared-reflective roofing granules according to claim 1 wherein the coating composition further comprises at least one coloring material selected from the group consisting of granule coloring pigments and uv-stabilized dyes.

Claim 6. Colored infrared-reflective roofing granules comprising base particles with size passing #8 mesh and retaining on #70 mesh coated with a cured coating composition comprising a coating binder and at least one colored, infrared-reflective pigment wherein the base particles comprise mineral particles coated with a cured base coating composition including a base particle binder, and at least one reflective white pigment.

Claim 7. Colored infrared-reflective roofing granules according to claim 6 wherein the at least one reflective white pigment is selected from the group consisting of titanium dioxide, zinc oxide and zinc sulfide.

Claim 8. Colored infrared-reflective roofing granules comprising base particles comprising inert mineral particles coated with a cured first coating composition including a base particle binder and at least one reflective white pigment, the base particles being coated with a cured second coating composition including a coating binder, and at least one colorant selected from the group consisting of uv-stabilized dyes and granule coloring pigments.

Claim 9. Colored infrared-reflective roofing granules according to claim 8, the colored infrared-reflective roofing granules having an L* value of less than 55.

Claim 10. Colored infrared-reflective roofing granules according to claim 8 the colored infrared-reflective roofing granules having an infrared reflectance of at least 25%.

Claim 11. Colored infrared-reflective roofing granules according to claim 8 wherein the second coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 12. Colored infrared-reflective roofing granules according to claim 8 wherein the at least one reflective white pigment is selected from the group consisting of titanium dioxide, zinc oxide and zinc sulfide.

Claim 13. Colored infrared-reflective roofing granules comprising inert mineral particles coated with a cured first coating composition including a base particle binder and at least one colorant selected from the group consisting of uv-stabilized dyes and granule coloring pigments to form base particles, the base particles being coated with a

cured second coating composition including a coating binder and at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 14. Colored infrared-reflective roofing granules according to claim 13, the colored infrared-reflective roofing granules having an L* value of less than 55.

Claim 15. Colored infrared-reflective roofing granules according to claim 13 the colored infrared-reflective roofing granules having an infrared reflectance of at least 25%.

Claim 16. Colored infrared-reflective roofing granules according to claim 13 wherein the first coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 17. A bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material and colored, infrared-reflective roofing granules comprising base particles with size passing #8 mesh and retaining on #70 mesh coated with a cured coating composition comprising a coating binder and at least one colored, infrared-reflective pigment.

Claim 18. A bituminous roofing product according to claim 17 having an L* value of less than 55.

Claim 19. A bituminous roofing product according to claim 17 having an infrared reflectance of at least 25%.

Claim 20. A bituminous roofing product according to claim 17 wherein the coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-

interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 21. A bituminous roofing product according to claim 17 wherein the base particles comprise mineral particles coated with a cured base coating composition including a base coating binder and at least one reflective white pigment.

Claim 22. A bituminous roofing product according to claim 21 wherein the at least one reflective white pigment is selected from the group consisting of titanium dioxide, zinc oxide and zinc sulfide.

Claim 23. A bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material and colored infrared-reflective roofing granules comprising base particles comprising inert mineral particles with size passing #8 mesh and retaining on #70 mesh coated with a cured first coating composition including a base particle binder and at least one reflective white pigment, the base particles being coated with a cured second coating composition including a coating binder, and at least colorant selected from the group consisting of uv-stabilized dyes and granule coloring pigments.

Claim 24. A bituminous roofing product according to claim 23 having an L* value of less than 55.

Claim 25. A bituminous roofing product according to claim 23 having an infrared reflectance of at least 25%.

Claim 26. A bituminous roofing product according to claim 23 wherein the second coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 27. A bituminous roofing product according to claim 23 wherein the at least one reflective white pigment is selected from the group consisting of titanium dioxide, zinc oxide and zinc sulfide.

Claim 28. A bituminous roofing product comprising a substrate sheet of a fibrous material saturated with a bituminous coating material and colored infrared-reflective roofing granules comprising inert mineral particles with size passing #8 mesh and retaining on #70 mesh coated with a cured first coating composition including a base particle binder and at least one colorant selected from the group consisting of uv-stabilized dyes and granule coloring pigments to form base particles, the base particles being coated with a cured second coating composition including a coating binder and at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, and mirrorized silica pigments based upon metal-doped silica.

Claim 29. A bituminous roofing product according to claim 28 having an L* value of less than 55.

Claim 30. A bituminous roofing product according to claim 28 having an infrared reflectance of at least 25%.

Claim 31. A bituminous roofing product according to claim 28 wherein the first coating composition further comprises at least one infrared-reflective functional pigment selected from the group consisting of light-interference platelet pigments including mica, light-interference platelet pigments including titanium dioxide, mirrorized silica pigments based upon metal-doped silica, and alumina.

Claim 32. A mineral surfaced asphalt shingle having $L^* < 60$ and solar reflectance $> 25\%$.

EVIDENCE APPENDIX

The evidence relied upon by the appellant includes a printout from the website of Chemalloy Corporation relating to powder sizes and providing a comparison of USA Sieve Series sizes and Tyler Standard Screen Scale Sieve Size equivalents. This printout was submitted with applicants' amendment of November 28, 2005 and is included in this Appendix as Exhibit A. US Patents 6,423,132 and 6,908,675 were also referenced in that amendment, and are included in this Appendix as Exhibits B and C.

EXHIBIT A



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POWDER SIZES

U.S.A. SIEVE SERIES and TYLER EQUIVALENTS
TYLER STANDARD SCREEN SCALE SIEVES

U.S.A. SIEVE SERIES and TYLER EQUIVALENTS

A. S. T. M.
-E-11-70

Sieve Designation		Sieve Opening		Nominal Wire Diameter		Tyler Screen Scale Equiv. Designation
Standard(a)	Alternate	mm	equiv- alent	mm	equiv- alent	
125 mm	5 in.	125	5	8	0.315	
106 mm	4.24 in.	106	4.24	6.4	0.252	
100 mm	4.0 in. (b)	100	4	6.3	0.248	
90 mm	3 1/2 in.	90	3.5	6.08	0.2394	
75 mm	3.0 in.	75	3	5.8	0.2283	
63 mm	2 1/2 in.	63	2.5	5.5	0.2165	
53 mm	2.12 in.	53	2.12	5.15	0.2028	
50 mm	2.0 in. (b)	50	2	5.05	0.1988	
45 mm	1 3/4 in.	45	1.75	4.85	0.1909	
37.5 mm	1 1/2 in.	37.5	1.5	4.59	0.1807	
31.5 mm	1 1/4 in.	31.5	1.25	4.23	0.1665	
26.5 mm	1.06 in.	26.5	1.06	3.9	0.1535	1.050 in.
25.0 mm	1.0 in. (b)	25	1	3.8	0.1496	
22.4 mm	7/8 in.	22.4	0.875	3.5	0.1378	.883 in.
19.0 mm	3/4 in.	19	0.75	3.3	0.1299	.742 in.
16.0 mm	5/8 in.	16	0.625	3	0.1181	.624 in.
13.2 mm	.530 in.	13.2	0.53	2.75	0.1083	.525 in.
12.5 mm	1/2 in. (b)	12.5	0.5	2.67	0.1051	
11.2 mm	7/16 in.	11.2	0.438	2.45	0.0965	.441 in.
9.5 mm	3/8 in.	9.5	0.375	2.27	0.0894	.371 in.
8.0 mm	5/16 in.	8	0.312	2.07	0.0815	2 1/2 mesh
6.7 mm	.265 in.	6.7	0.265	1.87	0.0736	3.0 mesh

6.3 mm	1/4 in. (b)	6.3	0.25	1.82	0.0717	
5.6 mm	No. 3 1/2 ©	5.6	0.223	1.68	0.0661	3 1/2 mesh
4.75 mm	No. 4	4.75	0.187	1.54	0.0606	4 mesh
4.00 mm	No. 5	4	0.157	1.37	0.0539	5 mesh
3.35 mm	No. 6	3.35	0.132	1.23	0.0484	6 mesh
2.80 mm	No. 7	2.8	0.111	1.1	0.043	7 mesh
2.36 mm	No. 8	2.36	0.0937	1	0.0394	8 mesh
2.00 mm	No. 10	2	0.0787	0.9	0.0354	9 mesh
1.70 mm	No. 12	1.7	0.0661	0.81	0.0319	10 mesh
1.40 mm	No. 14	1.4	0.0555	0.725	0.0285	12 mesh
1.18 mm	No. 16	1.18	0.0469	0.65	0.0256	14 mesh
1.00 mm	No. 18	1	0.0394	0.58	0.02285	16 mesh
850 um	No. 20	0.85	0.0331	0.51	0.0201	20 mesh
710 um	No. 25	0.71	0.0278	0.45	0.0177	24 mesh
600 um	No. 30	0.6	0.0234	0.39	0.0154	28 mesh
500 um	No. 35	0.5	0.0197	0.34	0.0134	32 mesh
425 um	No. 40	0.425	0.0165	0.29	0.0114	35 mesh
355 um	No. 45	0.355	0.0139	0.247	0.0097	42 mesh
300 um	No. 50	0.3	0.0117	0.215	0.0085	48 mesh
250 um	No. 60	0.25	0.0098	0.18	0.0071	60 mesh
212 um	No. 70	0.212	0.0083	0.152	0.006	65 mesh
180 um	No. 80	0.18	0.007	0.131	0.0052	80 mesh
150 um	No. 100	0.15	0.0059	0.11	0.0043	100 mesh
125 um	No. 120	0.125	0.0049	0.091	0.0036	115 mesh
106 um	No. 140	0.106	0.0041	0.076	0.003	150 mesh
90 um	No. 170	0.09	0.0035	0.064	0.0025	170 mesh
75 um	No. 200	0.075	0.0029	0.053	0.0021	200 mesh
63 um	No. 230	0.063	0.0025	0.044	0.0017	250 mesh
53 um	No. 270	0.053	0.0021	0.037	0.0015	270 mesh
45 um	No. 325	0.045	0.0017	0.03	0.012	325 mesh
38 um	No. 400	0.038	0.0015	0.025	0.001	400 mesh

(a) These standard designations correspond to the values for test sieve apertures recommended by the International Standards Organization Geneva, Switzerland.

(b) These sieves are not in the fourth root of 2 Series, but they have been included because they are in common usage.

(c) These numbers (3 1/2 to 400) are the approximate number of openings per linear inch but it is preferred that the sieve be identified by the standard designation in millimeters or um.

TYLER STANDARD

Tyler Standard	Closer Sizing	Mesh Designation	USA Sieve Series Equivalents
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**SCREEN
SCALE
SIEVES**

Scale Opening in Inches	Ratio Opening In inches		Standard Designation	Alternate Designation
1.05	1.05		26.5 mm	1.06 in.
	0.883		22.4 mm	7/8 in.
0.742	0.742		19.0 mm	3/4 in.
	0.624		16.0 mm	5/8 in.
0.525	0.525		13.2 mm	.530 in.
	0.441		11.2 mm	7/16 in.
0.371	0.371		9.5 mm	3/8 in.
	0.312	2.5	8.0 mm	5/16 in.
0.263	0.263	3	6.7 mm	.265 in.
	0.221	3.5	5.6 mm	No. 3 1/2
0.185	0.185	4	4.75 mm	No. 4
	0.156	5	4.00 mm	No. 5
0.131	0.131	6	3.35 mm	No. 6
	0.11	7	2.80 mm	No. 7
0.093	0.093	8	2.36 mm	No. 8
	0.078	9	2.00 mm	No. 10
0.065	0.065	10	1.70 mm	No. 12
	0.055	12	1.40 mm	No. 14
0.046	0.046	14	1.18 mm	No. 16
	0.039	16	1.00 mm	No. 18
0.0328	0.0328	20	850 um	No. 20
	0.0276	24	710 um	No. 25
0.0232	0.0232	28	600 um	No. 30
	0.0195	32	500 um	No. 35
0.0164	0.0164	35	425 um	No. 40
	0.0138	42	355 um	No. 45
0.0116	0.0116	48	300 um	No. 50
	0.0097	60	250 um	No. 60
0.0082	0.0082	65	212 um	No. 70
	0.0069	80	180 um	No. 80
0.0058	0.0058	100	150 um	No. 100
	0.0049	115	125 um	No. 120
0.0041	0.0041	150	106 um	No. 140
	0.0035	170	90 um	No. 170
0.0029	0.0029	200	75 um	No. 200
	0.0024	250	63 um	No. 230
0.0021	0.0021	270	53 um	No. 270
	0.0017	325	45 um	No. 235
0.0015	0.0015	400	38 um	No. 400

In the table of the Tyler Standard Screen Scale Sieve Series both the square root of two Series as well as the expanded series for closer sizing according to the fourth root of two as shown.

EXHIBIT B



US006423132B2

(12) **United States Patent**
Balliello et al.(10) **Patent No.:** **US 6,423,132 B2**
(45) **Date of Patent:** **Jul. 23, 2002**(54) **PIGMENT GRANULATION**(75) Inventors: **Paolo Balliello**, Rheinfelden (CH);
Horst Olaf Brücker, Rheinfelden (DE)(73) Assignee: **Ciba Specialty Chemicals Corporation**, Tarrytown, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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Primary Examiner—Anthony J. Green(74) *Attorney, Agent, or Firm*—David R. Crichton(57) **ABSTRACT**

The present invention is drawn to pigment granules having a particle size from 0.5 to 4 mm, which consist of at least 90% by weight of at least one organic pigment selected from the group consisting of diketopyrrolopyrrole, quinacridone, perylene, indanthrone, flavanthrone, isoindolinone or amino- anthraquinone pigments and from 0 to 10% by weight of a binder having from 2 to 7 mol of carboxyl groups per 1000 g and from 0 to 5% by weight of a neutral emulsifier. The binder and the emulsifier together do not represent more than 10% by weight of the overall amount of pigment granules. The pigment present in the pigment granules has a particle size of from 0.01 to μm .

18 Claims, No Drawings(21) Appl. No.: **09/783,902**(22) Filed: **Feb. 15, 2001****Related U.S. Application Data**

(62) Division of application No. 09/269,498, filed on Mar. 29, 1999, now Pat. No. 6,241,813.

(30) **Foreign Application Priority Data**

Oct. 22, 1996 (CH) 2580/96

(51) **Int. Cl.**⁷ **C09B 48/00**; C09B 67/20;
C09B 67/08; C09B 67/10; C09B 67/12(52) **U.S. Cl.** **106/493**; 106/494; 106/495;
106/496; 106/497; 106/498; 106/499(58) **Field of Search** 106/493, 494,
106/495, 496, 497, 498, 499(56) **References Cited****U.S. PATENT DOCUMENTS**

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PIGMENT GRANULATION

This is a divisional of application Ser. No. 09/269,498 filed Mar. 29, 1999, U.S. Pat. No. 6,241,813.

The invention relates to a novel process for granulating organic colour pigments in the presence of aqueous or alcoholic media at low pressure, and to the dust-free pigment granules which can be prepared by this process.

Organic pigments consist of very fine particles, of low solubility in customary solvents, whose dimensions can lie within the range from submicroscopic to about 100 μm . For practical use, organic pigments having approximate particle sizes of from 0.01 to 0.1 μm for transparent forms and from 0.1 to 10 μm for opacifying forms have proved most suitable.

The physical properties of the pigment particles are very important to their use. For instance, very small particles possess an often relatively low light fastness and fastness to weathering and a strong propensity to agglomeration. Very coarse particles, on the other hand, give rise to undesirably low colour intensities and duller shades. In the case of the physical properties, however, particle size distribution and agglomeration play a key part, especially with respect to the dispersibility of the pigments [cf. Farbe und Lack 82/1, 7–14 (1976)].

It is therefore of critical importance for pigments to have a very narrow particle size distribution, which can usually be achieved by reprecipitation, recrystallization or heat treatment in a polar solvent, at atmospheric or superatmospheric pressure or under a high shear force (U.S. Pat. No. 4,879, 380). However, all such pigments, irrespective of the narrow particle size distribution, still have the great disadvantage of producing dust. Consequently, when they are used, expensive measures (for example of a workplace safety, ecological or quality assurance nature) are necessary and valuable material is lost.

A very large number of methods have therefore already been investigated for converting the pigments into a low-dust or even dust-free form. It has however been found that improvements in the dusting behaviour can be obtained in the case of the known methods only, among other disadvantages, at the expense of the physical properties of the pigment particles, and especially at the expense of the dispersibility. Consequently, the known methods described below are unable to satisfy fully the long-held wish for dust-free organic pigments which continue to have good physical properties.

Known compacting methods, such as compression moulding (tableting or briquetting), granulation in mix granulators and granulating discs (Aufbereitungs-Technik 12 (1975)) and in formers (Chem.-Ing.-Tech. 49/5, 374–380 (1977)), roll granulation (DE-A 27 23 221) or pressure granulation (Powder Technology 74, 1–6 (1993)) always lead, with pure organic pigments, to highly agglomerated products having performance properties worse than those of the powder. A common feature of these methods is that the pigment particles collide with one another with a relatively high force.

Pigments for use in plastics can be incorporated into polymer concentrates. The pigment is employed as a dry, dusting powder. In this context, high shear forces and temperatures are required to disperse the pigment particles thoroughly, and the physical properties and colour properties are changed. The resulting polymer grains must in turn be mixed intimately with uncoloured polymer grains for the end use, again under high shear force, since it is necessary to effect homogeneous distribution of the pigment particles

together with the completely surrounding polymer. Moreover, the concentrate polymer must be compatible with the other polymer, which is why, for a single pigment, a range of two or more products is required for different plastics applications.

Pigments can also be applied to the surface of externally softened polymer granules to give spherical particles (U.S. Pat. No. 4,310,483). However, the size of such particles is difficult to control, and the fraction having the desired diameter has to be isolated by sieving. It is said that the granulating auxiliary can be used in amounts of 2–50% by weight (preferably 5–30% by weight), although it has been found that good dispersibility can only be achieved with amounts of at least 15–20% by weight. An additive which can be used in addition to the polymer granules is a wax-like binder whose melting point is typically from 49 to 88° C. (U.S. Pat. No. 5,455,288). In the latter case, however, the pigment content is at an unsatisfactorily low level of from 5 to 50%. In both cases, collision forces are principally at work in the case of low shear forces, and the presence of more than 10% by weight of a substance of low melting point is disadvantageous from the performance standpoint.

Pigments can also be embedded in resins. This is done by first preparing a dispersion of the pigment in an inert solvent (for example water) and a solution of the resin in an appropriate solvent and then mixing the two, and precipitating the resin from the solution, either directly in the course of mixing or else later, the pigment being enveloped by the precipitating resin. Innumerable publications have proposed, as the resin, almost all substances known to have a certain resinous character, including rosin. Various processes in accordance with this principle are known, for example acid/base precipitations (CS 216 590; IN 156 867; DE-A 33 27 562) and one- or two-phase solvent granulations (U.S. Pat. No. 4,055,439; U.S. Pat. No. 4,208,370). The not entirely satisfactory dispersibility of such resin-embedded pigments can be improved by the use of special resin mixtures coupled with a very high shear force (U.S. Pat. No. 4,116,924; U.S. Pat. No. 4,168,180). Nevertheless, the preparation of the pigment dispersion in any case requires intensive milling, especially when the inert solvent used is an aqueous medium, in which case the pigment, however, is comminuted in an undesirable manner. Instead of resins it is also possible to use surfactants (EP 403 917): in this case, although dispersion is made easier, the product is not obtained in a dust-free form but rather in a powder form.

In the case of the acid/base precipitations, the control of neutralization is a further problem which cannot be solved with complete satisfaction by the method described in DE 33 27 562. When precipitating with acid, in fact, the resin does not precipitate in a completely neutral form, which in many cases causes problems for high-grade applications, such as coating operations or the mass colouring of plastics. In the case of solvent granulations, on the other hand, large amounts of solvents are required which, disadvantageously, have to be recovered from usually aqueous mixtures. Therefore, the use of acetic or propionic anhydride as solvent has been proposed (EP 069 617), giving rise to aqueous solutions which can purportedly be used in the chemical industry but which, for lack of demand, have to be disposed of at considerable cost.

It is also known that colorants can be converted into a low-dust flowable form by spray-drying or in a fluidized bed (EP 039 841; EP 670 352). The additives used therein, however, are completely unusable in the case of pigments that are to be used in high-grade applications such as the mass colouring of plastics or automotive finishing opera-

tions. Moreover, in the case of spray-drying or in a fluidized bed it is hardly possible to prepare homogeneous granules having a particle size of more than a few 100 μm (cf. e.g. *Chemie-Technik* 21/6, 72–78 (1992); *Arch. Pharm. Chemi. Sci. Ed.* 1978/6, 189–201). Furthermore, it is not possible to fluidize all powders in a fluidized bed (*Powder Technology* 57, 127–133 (1989)), so that it is in no way possible to make generalized use of this method.

An improved variant of fluidized bed granulation, especially for pigments, is also known (U.S. Pat. No. 4,264,552) where the particle size distribution of these granules is very broad and the great majority of the particles (about half by weight) are smaller than 500 μm . Furthermore, these granules still have an excessive propensity to produce dust. In Example 2 the use is disclosed of a mixture of 8.2% by weight of Staybelite ResinTM and 0.9% by weight of hydroxypropylcellulose (amounts based in each case on the finished product), in the form of its ammonium salts, as the anionic surfactant.

Water-soluble dyes can be processed with from 5 to 50% by weight of a water-soluble binder to form non-dusting cylindrical granules with a diameter of at least 1 mm (DE-A 2 317 175); according to the examples the granules have a diameter of about 1 mm and a length of 5–7 mm. By means of a conveying screw, the homogeneous plastic mass is pressed through a perforated disc (perforation diameter 1 mm). However, water-soluble binders are completely unsuitable for pigments that are intended for use in customary plastics, and organic pigments treated by this process are highly agglomerated and have unsatisfactory dispersibility properties. They are therefore not sufficiently suitable for many applications. The same applies to the powder compression of water-moist pigments in a twin-screw extruder at pressures from 10 to 50 bar in accordance with the method known from *Journal of Powder & Bulk Solids Technology* 4/4, 27–32 (1980).

Also known are fine, low-dust colorant granules having a very low content of wax-like binder and other foreign substances (EP 424 896). Of essential importance is the use of a device in which the material fed in is exposed predominantly to severe turbulence and moderate collision forces coupled with declining shear stresses. This process is suitable, however, predominantly for inorganic pigments, and only one example of an organic pigment is disclosed: Example 13 uses the monoazo pigment Pigment Red 176, 0.72% by weight of a fatty acid mixture having a melting point of 57–61° C. as the wax, and 50–51% by weight of water (based in each case on the fine granules). The particle size is markedly less than 1 mm, and a sieving operation is necessary despite the relatively small proportions of coarse particles, which are difficult to disperse, and ultrafine particles, which produce dust.

Other known granules include those which exhibit a large increase in volume relative to the initial pigment as a result of the cavities which are retained on drying (EP 510 392). In this case shaping takes place exclusively by known methods; for extrusion to strands a residual moisture content of 50 to 80% by weight is specified. These granules are said to be readily dispersible and low in dust, but are brittle and have a low bulk density, with the result that they take up a substantially greater volume on transportation and storage. Furthermore, it is very difficult to obtain products having a precisely reproducible specific weight, and in the case of hydrophobic or apolar pigments this method produces unsatisfactory results.

Also known, finally, is a process in which hydrophilic pigments are transported as aqueous, paste-like agglomer-

ates (U.S. Pat. No. 5,328,506). In contrast to extruded “noodles” it is not necessary to carry out high-energy dispersion of these products later on. However, the process is aimed not at organic pigments but at inorganic kaolin pigments, and the presence of water in the stated amount of 1 to 25% has an adverse effect on, or may even rule out totally, the use of organic pigments in the vast majority of fields.

Furthermore, as already mentioned, the coarsely particulate pigment preparations prepared by some of the known processes are still not, simultaneously, satisfactorily compact, dust-free and/or readily dispersible. In addition, the desired particle size usually has to be selected by sieving, with particles having a size other than this desired particle size (especially the fine fraction) having to be passed back to the process. However, the recycling of the unsatisfactory pigment material causes an additional detrimental alteration to its physical parameters, and, consequently, a worsening in the performance properties as well.

The aim of the invention was to provide coarsely particulate, extremely dust-free, highly concentrated, readily dispersible and universally applicable organic pigment granules in which, apart from the external aspect, the physical parameters of the pigment particles are changed as little as possible relative to the initial pigment powder, unlike the known granules. The term physical parameters is understood as meaning not only the abovementioned properties but also all other technically measurable or applications-relevant properties. The intention is that these pigment granules should as far as possible be able to be prepared by means of simple and universally applicable methods, in simple, inexpensive and easy-to-clean apparatus, without the addition of organic solvents to be absolutely necessary and without the need to select the right particles and recycle the rejects.

The aim of the invention has been achieved to a particularly surprising extent by means of the present invention.

The invention relates to a process for preparing organic pigment granules with a particle size from 0.5 to 4 mm, which consist of at least 90% by weight of at least one organic pigment with a particle size from 0.01 to 10 μm and from 0 to 10% by weight of a binder having from 2 to 7 mol of carboxyl groups per 1000 g and from 0 to 5% by weight of a neutral emulsifier which does not form ions and which dissolves to give a clear solution in water or a C₁–C₄ alcohol at a concentration of at least 10 g/100 ml, the binder and the emulsifier together accounting for not more than 10% by weight and all percentages by weight being based on the overall amount of pigment granules, wherein

[1] the pigment is mixed with 54–92% by weight of water, a C₁–C₄ alcohol, a C₃–C₈ ketone or a mixture thereof, based on the dry pigment, with the binder and 0.8–20 mol of ammonia or a C₁–C₃ amine, per mole of carboxyl groups in the binder, and with the emulsifier;

[2] this mixture is pressed in a continuously operating apparatus through one or more apertures each having a size of 0.2–5.0 mm², the apparatus consisting of at least one conveying device and a shaping section comprising the apertures, and being constructed, and operated with a throughput, such that the pressure in its shaping section does not exceed 10 bar;

[3] if desired, the cylindrical granules emerging from the dies are converted on a rotating device into ovoid or spherical granules, and

[4] the granulated product is dried at a temperature of –50 to 200° C. at atmospheric pressure or under reduced pressure.

The granules can have any desired geometric form; for example, they can be cylindrical, ovoid or spherical. The

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granules preferably have a non-angular, rounded geometric form. With particular preference the granules are essentially spherical, which can be achieved by the optional step [3]. If spherical, the granules generally have a particle size with a diameter from 0.5 to 4 mm. Cylindrical and ovoid granules generally have a diameter from 1 to 3 mm and a length from 1 to 10 mm.

The granules preferably have a particle size with a diameter from 1 to 4 mm. With particular preference the granules have a particle size with a diameter from 1 to 2.5 mm. If the granules are not spherical, they have a particle size with a theoretical diameter

$$\left(\sqrt[3]{\frac{6 \times \text{volume}}{\pi}} \right)$$

from 1 to 2.5 mm.

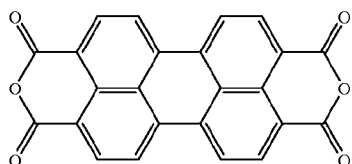
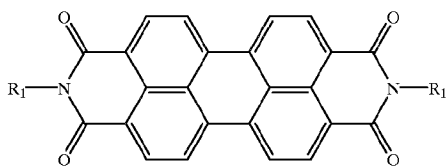
Within the granules, the organic pigment and the binder preferably form an essentially homogeneous mixture.

The organic pigment can be an individual compound from any desired pigment class, or else a mixture of two or more compounds from the same or from different pigment classes, and can be present in any desired, known crystal modification, which is advantageously retained in the course of the process of the invention, or else can be a solid solution.

Examples of suitable pigment classes are the diketopyrrolopyrroles, quinacridones, perylenes, dioxazines, anthraquinones, indanthrones, flavanthrones, indigos, thioindigos, quinophthalones, isoindolinones, isoindolines, phthalocyanines, metal complexes and azo pigments.

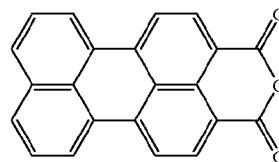
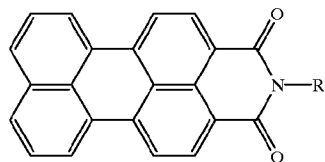
Preferred pigments are diketopyrrolopyrroles, quinacridones, perylenes, dioxazines, indanthrones, flavanthrones, isoindolinones and phthalocyanines and also aminoanthraquinones and disazo condensation pigments. Particularly preferred pigments are diketopyrrolopyrroles, quinacridones and phthalocyanines. Very particularly preferred pigments are diketopyrrolopyrroles.

Preferred perylenes are of the formula (Ia), (Ib), (Ic) or (Id),



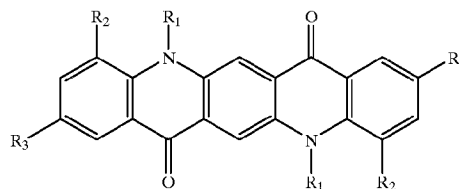
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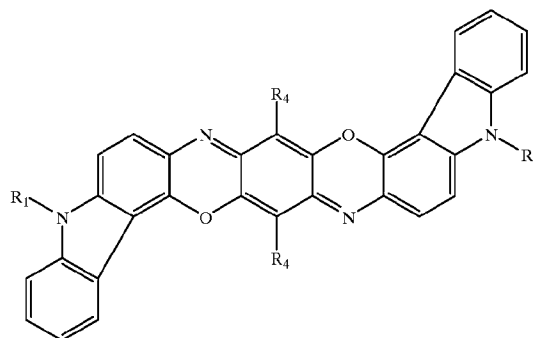
in which R₁ is hydrogen, C₁–C₆alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C₁–C₄alkyl or C₁–C₄alkoxy.

Preferred quinacridones are of the formula (II),



in which R₁ is hydrogen, C₁–C₆alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C₁–C₄alkyl or C₁–C₄alkoxy, and R₂ and R₃ independently of one another are hydrogen, halogen, C₁–C₁₈alkyl, C₁–C₄alkoxy or phenyl.

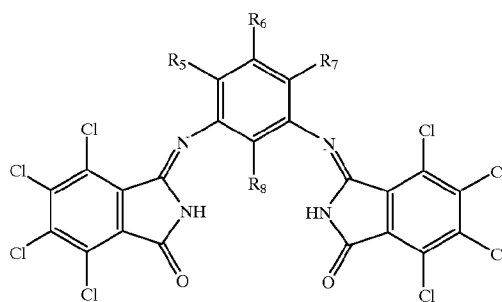
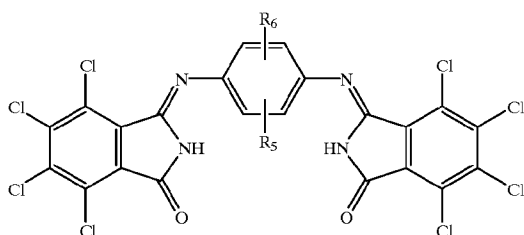
Preferred dioxazines are of the formula (III),



in which R₁ is hydrogen, C₁–C₆alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C₁–C₄alkyl or C₁–C₄alkoxy, and R₄ is hydrogen, halogen or C₁–C₁₈alkyl.

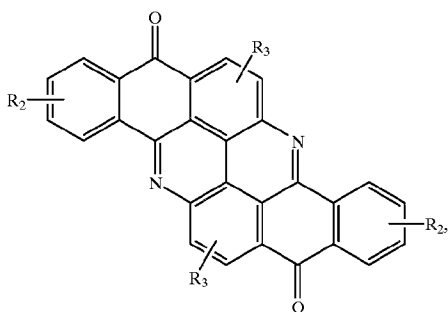
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Preferred isoindolinones are of the formula (IVa) or (IVb),



in which R_5 , R_6 , R_7 and R_8 independently of one another are hydrogen, C_1 - C_{18} alkyl, C_1 - C_4 alkoxy, halogen or trifluoromethyl.

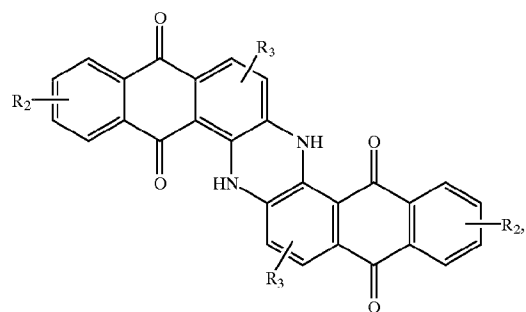
Preferred flavanthrones are of the formula (V),



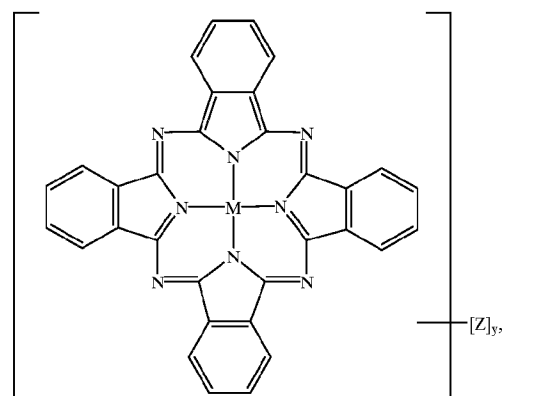
in which R_2 and R_3 independently of one another are hydrogen, halogen, C_1 - C_{18} alkyl, C_1 - C_4 alkoxy or phenyl.

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Preferred indanthrones are of the formula (VI),

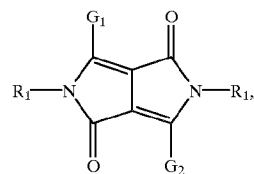


in which R_2 and R_3 independently of one another are hydrogen, halogen, C_1 - C_{18} alkyl, C_1 - C_4 alkoxy or phenyl.
Preferred phthalocyanines are of the formula (VII),

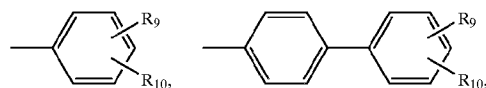


in which M is H_2 , Zn, Cu, Ni, Fe, $Ti(=O)$ or $V(=O)$,
Z is halogen and
y is 0 or an integer from 1 to 4.

Preferred pyrrolo(3,4-c)pyrroles are of the formula (VIII),

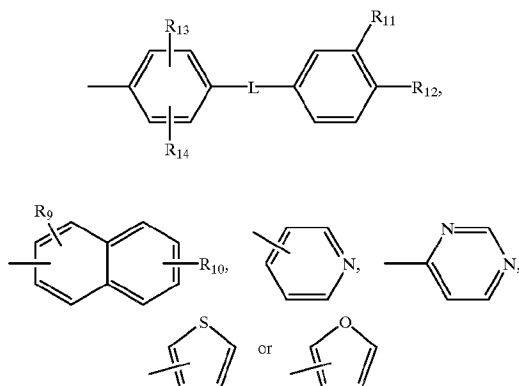


in which R_1 is hydrogen, C_1 - C_6 alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, and
 G_1 and G_2 independently of one another are a group of the formula

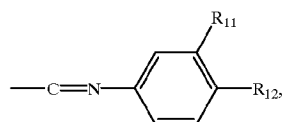


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in which R₉ and R₁₀ independently of one another are hydrogen, halogen, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₁₈alkylamino, C₂-C₁₈dialkylamino, —CN, —NO₂, phenyl, trifluoromethyl, C₅-C₆cycloalkyl, imidazolyl, pyrazolyl, triazolyl, piperazinyl, pyrrolyl, oxazolyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, morpholinyl, piperidinyl, pyrrolidinyl, —C=N— (C₁-C₁₈alkyl) or



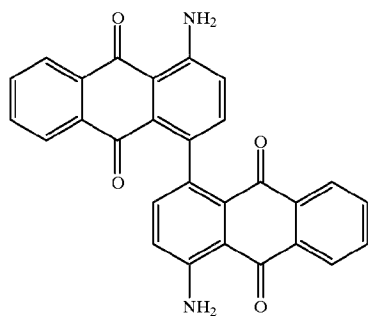
R₁₁ and R₁₂ independently of one another are hydrogen, halogen, C₁-C₆alkyl, C₁-C₆alkoxy or —CN,

R₁₃ and R₁₄ independently of one another are hydrogen, halogen or C₁-C₆alkyl,

L is —CH₂—, —CH(CH₃)—, —C(CH₃)₂—, —CH=N—, —N=N—, —O—, —S—, —SO—, —SO₂— or —NR₁₅—, and

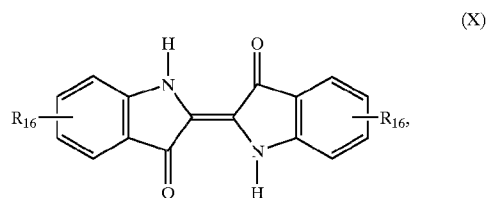
R₁₅ is hydrogen or C₁-C₆alkyl.

The preferred aminoanthraquinone pigment is of the formula (IX)



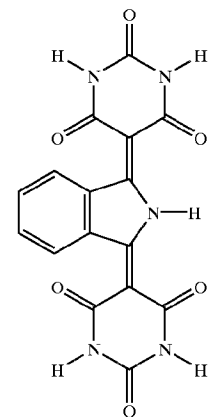
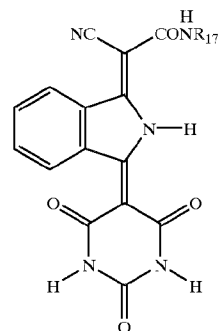
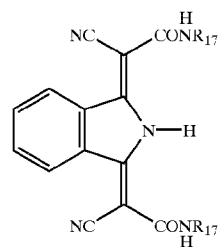
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Preferred indigo derivatives are of the formula (X),



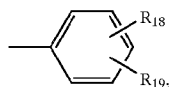
in which R₁₆ is hydrogen, CN, C₁-C₄alkyl, C₁-C₄alkoxy or halogen.

Preferred isoindolines are of the formula (XIa), (XIb) or (XIc),



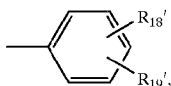
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in which R_{17} is hydrogen, C_1 - C_{18} alkyl, benzyl or a group



and

R_{17}' is a group



where R_{18} , R_{19} , R_{17}' and R_{18}' independently of one another are hydrogen, C_1 - C_{18} alkyl, C_1 - C_4 alkoxy, halogen or trifluoromethyl.

Any halogen substituents are, for example, iodine, fluorine, especially bromine and preferably chlorine.

C_1 - C_4 Alkyl is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl, in the case of C_1 - C_6 alkyl additionally, for example, n-amyl, tert-amyl or hexyl, and in the case of C_1 - C_{18} alkyl again additionally, for example, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl.

C_5 - C_6 Cycloalkyl is, for example, cyclopentyl and, in particular, cyclohexyl.

C_1 - C_4 Alkoxy is, for example, methoxy, ethoxy, n-propoxy, isopropoxy or butyloxy, and C_1 - C_{18} alkoxy is in addition, for example, hexyloxy, decyloxy, dodecyloxy, hexadecyloxy or octadecyloxy.

C_1 - C_{18} Alkylthio is, for example, methylthio, ethylthio, propylthio, butylthio, octylthio, decylthio, hexadecylthio or octadecylthio.

C_1 - C_{18} Alkylamino is, for example, methylamino, ethylamino, propylamino, hexylamino, decylamino, hexadecylamino or octadecylamino.

C_2 - C_{18} Dialkylamino is, for example, dimethylamino, diethylamino, methylpropylamino, ethylhexylamino, methyldecylamino, dioctylamino or ethylhexadecylamino, the carbon atoms of both alkyl radicals being counted together.

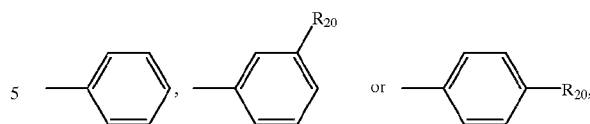
In the case of the perylenes of the formula (Ia) or (Ic), the quinacridones of the formula (II), the dioxazines of the formula (III) and the pyrrolo(3,4-c)pyrroles of the formula (VIII) particular preference is given to those in which R^1 is hydrogen.

Particularly preferred quinacridones of the formula (II) are those in which R_1 is hydrogen and R_2 and R_3 independently of one another are hydrogen, methyl, chlorine or methoxy.

Particularly preferred phthalocyanines of the formula (VII) are those in which M is H_2 , Zn or Cu, and Z is chlorine or bromine.

Particularly preferred pyrrolo(3,4-c)pyrroles of the formula (VIII) are those in which R_1 is hydrogen and G_1 and G_2 independently of one another are each a group of the formula

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in which

R_{20} is fluorine, chlorine, cyano, nitro, trifluoromethyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino or C_1 - C_4 dialkylamino, and, of these, especially those in which R_{20} is chlorine. A preference quite out of the ordinary is given to 1,4-diketo-3,6-di(4'-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole.

The organic pigment used in accordance with the invention has a particle size from 0.01 to 10 μm . This means that at least 90% by weight of the particles have this particle size. The organic pigment preferably has a mean particle size of from 0.2 to 2 μm . With particular preference the organic pigment has a narrow particle size distribution, in other words at least 80% by weight of the particles have a particle size which is within a range whose extent is not more than one power of ten, for example between 0.5 and 5 μm or between 0.2 and 2 μm . A narrow particle size distribution can be obtained by methods known to the skilled worker, for example by treatment in a polar inert liquid at elevated temperature. Appropriate liquids, temperatures and durations for this treatment, which may be very different depending on the pigment, are known for all pigment classes and for many individual pigments.

The binder has from 2 to 7 mol of carboxyl groups per 1000 g of substance. The binder generally contains 30-100% by weight, preferably at least 60% by weight, of at least one organic acid, it being possible for the remainder of the binder to be neutral. The organic acid can, for example, be a saturated or unsaturated, long-chain pure acid, or a mixture thereof, for example a homologue mixture. Long-chain acids are those in which there is at least one linear chain consisting of 8 C atoms. Preference is given to abietic acid and to acid mixtures comprising at least 5% by weight of abietic acid.

The neutral remainder of the binder may comprise, for example, substances which usually appear as impurities in the acids used. However, it is likewise possible to add relatively small amounts of a texture enhancer to the organic acid. The texture enhancer, if added, is a constituent of the binder; its amount is not more than 50% by weight, preferably not more than 10% by weight, based on the overall binder. The texture enhancer can, for example, be an amide or a metal salt of an organic acid having at least 18 C atoms, an alkylphenol or an aliphatic alcohol, or a plasticizer or a wax. Known texture enhancers are, for example, stearamide or behenamide, magnesium stearate or magnesium behenate, stearyl alcohol, aliphatic 1,2-dihydroxy compounds having 8 to 22 C atoms, such as 1,2-dodecanediol, dibutyl phthalate or beeswax.

The binder consists preferably of a mixture of naturally occurring acids having 8 to 30 carbon atoms and naturally occurring terpene derivatives, and can be obtained, for example, by extraction from naturally occurring woods. For example, this mixture can be resin or Staybelite ResinTM (Hercules Inc., Wilmington/Del./USA). The binder particularly preferably has a melting point of 70-300° C. and, with very particular preference, a melting point of 90-200° C.

The exact amount of the binder depends on what is required of the granules. If granules with very high mechanical loadability are required, then the amount of binder is

preferably 5–10% by weight, particularly preferably 5–8% by weight. If, on the other hand, universal granules of very good compatibility in as wide as possible a range of applications (for example in coatings) are desired, then the amount of binder is preferably 0.5–2% by weight. Very particular preference is given to granules which contain less than 0.5% by weight of binder or which are even totally free from binder. Although in the latter case it is unclear how the pigment particles are held together within the granules, it has been found, very surprisingly, that even binder-free granules prepared in accordance with the invention have a highly remarkable mechanical stability.

The neutral non-ionic emulsifier can be, for example, a copolymer of ethylene oxide and propylene oxide, a fatty alcohol ethoxylate or an alkylphenol ethoxylate, for example an emulsifier of the Emulan® series (BASF). The amount of emulsifier is preferably 0.3–1% by weight.

Binder and emulsifier are independent of one another and both are optional. Depending on the desired granule properties it is possible to use, as desired, binder, emulsifier, both binder and emulsifier, or neither binder nor emulsifier. The binders and emulsifiers listed are used in the process according to the invention, if at all, in the stated concentrations, which begin at zero per cent by weight (corresponding to complete absence). The preferred overall amount of binder and emulsifier is preferably 0.3–5% by weight.

The C_1 – C_8 alcohol may be if desired, for example, methanol, ethanol, n-propanol, isopropanol or a butanol, and can be used in pure form or, in particular, as aqueous mixtures. Preference is given to C_1 – C_4 alcohols, especially methanol, ethanol or isopropanol; methanol is particularly preferred.

The C_3 – C_8 ketone may be if desired, for example, acetone, ethyl methyl ketone, methyl propyl ketone or cyclohexanone, and can be used in pure form or, in particular, as aqueous mixtures. Preference is given to C_3 – C_6 ketones, especially acetone or ethyl methyl ketone; ethyl methyl ketone is particularly preferred.

However, it is generally very particularly preferred to use in stage [1] from 90 to 100% by weight of water, based on the overall amount of water, C_1 – C_8 alcohol and C_3 – C_8 ketone, it being possible to use, in particular, water alone, which can for example be of a defined quality, for example deionized water. As an exception, highly polar pigments such as pigments having at least one primary amino group, for example the aminoanthraquinone of formula (IX), are preferably granulated at a lower concentration of water, particularly preferred at from 30 to 60% by weight of water, based on the overall amount of water, C_1 – C_8 alcohol and C_3 – C_8 ketone.

If a mixture of water, a C_1 – C_8 alcohol and/or a C_3 – C_8 ketone is used, it is preferably an azeotropic mixture. This makes it possible to reuse the mixture easily in an advantageous manner.

The C_1 – C_3 amine may, if desired, be methylamine, dimethylamine, ethylamine, trimethylamine, ethylmethylamine, n-propylamine or isopropylamine. Preference is given to C_1 – C_3 amines having a very low boiling point, and particular preference to methylamine. With very particular preference, however, ammonia rather than a C_1 – C_3 amine is used in stage [1]. Ammonia is understood as meaning gaseous ammonia; instead it is of course also possible to use liquid ammonia—in this case, however, the water of the liquid ammonia also counts as added water. The preferred amount of ammonia or C_1 – C_3 amine is about 1 mol per mole of carboxyl groups in the binder, so that the binder is just completely neutralized.

The mixing of the pigment with the water and/or C_1 – C_8 alcohol and/or with the C_3 – C_8 ketone, the emulsifier, the binder and the ammonia or C_1 – C_3 amine can be effected in any known manner, for example in a mixing apparatus. Useful mixing apparatus is that in which the pigment is subjected to a maximum pressure which is lower than the maximum pressure arising in stage [2] of the process. The skilled worker is aware of numerous mixers imposing little mechanical stress, for example those described in Perry's Chemical Engineer's Handbook (6th Ed., McGraw-Hill Book Company). Commercially available annular bed mixers are preferred.

The pigment can be employed in dry form or else in the form of moist product, for example a moist filter cake; in the latter case, the water or C_1 – C_8 alcohol or C_3 – C_8 ketone present in the moist product also counts as added water or alcohol or ketone. If the moist product is sufficiently moist it may be possible to do entirely without additional moistening media. For example, a pigment filter cake with 47.9% residual moisture corresponds to the addition of 91.9% by weight, and one with 35.1% residual moisture to the addition of 54.1% by weight, of water to the dry pigment. Preferably, however, a dry pigment of known specifications is employed. The binder can be employed dry or in the form of a solution of the ammonium salt. In the latter case, for example, the binder is stirred beforehand together with ammonia or a C_1 – C_3 amine in water, C_1 – C_8 alcohol, C_3 – C_8 ketone or a mixture thereof, at room temperature or at a temperature which is between room temperature and the melting point of the binder, under atmospheric or superatmospheric pressure, until a solution is formed. Binder solutions are preferably prepared at room temperature.

The form and sequence in which the ingredients are mixed in is essentially unimportant. What is important, however, is that the mixture is substantially homogeneous after mixing. It is therefore preferred to employ the binder in the form of a solution of the ammonium salt, in which case all of the water or C_1 – C_4 alcohol, or just part of it, can be used to prepare this solution.

It is particularly preferred to meter in the dry pigment continuously at the entrance of the mixer while at the same time spraying on an ammoniacal aqueous solution of the binder in the required amount. This process lends itself particularly well to full automation by methods known per se. The mixed product can be processed further immediately or later in stage [2] of the process, it being preferred to follow stage [1] directly by stage [2].

Pressing takes place mechanically in a continuously operating apparatus which consists at least of a conveying device and a shaping section with apertures. The conveying device is not subject to any particular requirements, other than that the mixture to be pressed should not be subjected therein to any pressure exceeding 10 bar. Conventional conveying devices can be used, for example one or more rotating screws. A twin screw is the preferred conveying device.

The apertures through which the mixture is pressed can in principle have any desired cross-section. Apertures with a non-angular cross-section are preferred. By this are meant rounded, for example elliptical or, preferably, circular apertures which have no angles. The apertures preferably measure from 0.5 to 2.5 mm in the shortest axis. The apertures can, for example, be punched out or burnt with a laser beam, while the circular apertures can in addition, and preferably, be drilled. It is preferred to have a large number of apertures made at regular intervals. The preferred diameter of circular apertures is dependent on the binder and at 0–3% by weight of binder is from 0.5 to 1.5 mm, at 3–10% by weight of binder, on the other hand, from 1.0 to 2.5 mm.

The shaping section with the apertures has any desired form which is neither planar nor cylindrical. If use is made in fact of a planar sieve arranged at right angles to the conveying device, then the pressure generally exceeds the maximum pressure which is critical to the invention, and the granules do not have the advantages of the invention. It is therefore critical for the shaping section with the apertures to have a three-dimensional curvature, for example a hollow truncated cone or a hollow dome. On the other hand, the material to be shaped is often pressed in a highly irregular manner if the sieve is a hollow cylinder, and in this case increases in pressure, possibly exceeding the maximum pressure which is critical to the invention, occur readily for short periods, and at least some of the material likewise lacks the advantages of the invention. The shaping section is preferably hemispherical.

The preferred apparatus constructed in accordance with the features of the invention comprises radial extruders and, with particular preference, dome extruders, which are obtainable commercially in numerous designs. Since the build-up of pressure is a function of the rotational speed of the conveying screw, the apparatus should be operated at a lower rotational speed than the maximum speed, corresponding to a reduced throughput, where this appears necessary on the basis of the desired maximum pressure.

In a radial extruder the pressure increases in the direction of the cone apex. In this case it may be that the pressure at the apex of the shaping section threatens to exceed 10 bar. In general, therefore, the apex of the shaping section should have an additional aperture, which should be designed or set such that the desired pressure is not exceeded. The small amount of material emerging from this additional regulatable aperture can in fact be recycled but only if it has been exposed to a maximum pressure of not more than 10 bar. Recycling, however, is generally not advisable. This problem does not arise in the case of the dome extruder, which is particularly preferred.

The pressure in the shaping section is preferably from 1 to 5 bar, particularly preferably from 1.1 to 3 bar. The cylindrical extrudate generally breaks up of its own accord on emergence from the shaping section into pieces with a length of about 2 to 6 mm, which judiciously should not be allowed to stand for any length of time. The cylindrical granules are preferably processed further directly.

The rotating device which converts the cylindrical granules into spherical granules can be, for example, a plate, a hollow cylinder or the like. The cylindrical material emerging from the extruder is preferably passed directly onto roughly the centre of the rotating device, centrifugal force setting the cylindrical granules into a rolling movement and so converting them into more or less spherical granules.

Conversion into ovoid or spherical granules is optional. However, it has been found that the performance advantages of the invention are greater if the granules are ovoid or spherical. Preferably, therefore, this optional stage is implemented.

The granulated product is dried in known manner at the stated temperature and under the stated pressure. Drying can be operated batchwise or continuously, in the latter case the material to be dried being conveyed, for example on a conveyor belt, through an oven which is open at both ends and is at a temperature of 100–200° C. In the course of drying both the water or the C_1 – C_4 alcohol and, if present, the ammonia or the C_1 – C_3 amine are released, and are stripped off if necessary. The vapours are preferably taken off under suction and condensed, with the condensates being recycled. Instead of drying in an oven, however, it is also possible to use any other drying method, for example freeze-drying.

The whole of the process of the invention is preferably operated continuously.

The pigment granules prepared in accordance with the invention are coarse and highly concentrated, extremely dust-free and readily dispersible. The physical parameters of the pigment particles present within the pigment granules are hardly changed relative to those of the pigment particles in the initial pigment powder. In general, therefore, organic pigment present in the pigment granules likewise has a particle size of from 0.01 to 10 μ m. The organic pigment enclosed in the pigment granules preferably has a narrow particle size distribution. Further preferred pigment granules include those obtained by the abovementioned preferred embodiments of the process of the invention.

The invention therefore also relates to pigment granules with a particle size from 0.5 to 4 mm which consist of at least 90% by weight of at least one organic pigment and from 0 to 10% by weight of a binder having from 2 to 7 mol of carboxyl groups per 1000 g and from 0 to 5% by weight of a neutral emulsifier which does not form ions and which dissolves to give a clear solution in water or a C_1 – C_4 alcohol at a concentration of at least 10 g/100 ml, the binder and the emulsifier together accounting for not more than 10% by weight and all percentages by weight being based on the overall amount of pigment granules, wherein the pigment present in the pigment granules essentially has a particle size of from 0.01 to 10 μ m.

To determine the particle size of the pigment present therein, the granules can be treated with ultrasound in a liquid which wets but does not dissolve the pigment, but which may dissolve or break up the other components of the granules, so as to give a homogeneous dispersion of the pigment. The particle size distribution of the dispersed pigment can then be determined, for example, by disc centrifuging. A suitable apparatus for this, for example, is the Joyce-Loebl disc centrifuge DCF 4. The requirements regarding sample preparation and the determination of the particle size distribution are very well known to the skilled worker in the field of particle measurement. The techniques are also described comprehensively in relevant textbooks [cf. e.g. Terence Allen, Particle Size Measurement, (Chapman and Hall, London, New York 1981)].

On account of the properties highlighted above, the pigment granules of the invention are especially suitable, in an effective amount for colouring, for pigmenting high molecular mass organic material, especially plastics and coatings.

The high molecular mass organic material for whose pigmenting the pigment granules of the invention can be used can be of natural or synthetic origin. High molecular mass organic materials usually have molecular weights from about 10^3 to 10^7 g/mol or more. They may be, for example, natural resins, drying oils, rubber or casein or natural substances modified from these, such as chlorinated rubber, oil-modified alkyd resins, viscose, cellulose ethers or esters, such as ethylcellulose, cellulose acetate, cellulose propionate, cellulose acetobutyrate or nitrocellulose, but especially fully synthetic organic polymers (thermosets and thermoplastics) as are obtained by addition polymerization, condensation polymerization or polyaddition. From the class of the addition polymerization resins mention may be made primarily of polyolefins, such as polyethylene, polypropylene or polyisobutylene, and substituted polyolefins, such as polymers of vinyl chloride, vinyl alcohol, vinyl acetate, butyl acetate, styrene, acrylonitrile, acrylic or methacrylic acid, acrylic or methacrylic esters or butadiene, and also copolymers of the monomers mentioned, especially ABS or EVA.

From the series of the polyaddition resins and condensation polymerization resins mention may be made of the condensates of formaldehyde with phenols, known as phenolic resins, and the condensates of formaldehyde with urea, thiourea and melamine, known as aminoresins, the polyesters which are used as paint resins, and indeed both saturated resins, for example alkyd resins, and unsaturated resins, for example maleate resins, and also the linear polyesters and polyamides, polyurethanes or silicones.

The high molecular mass compounds mentioned can be present individually or in mixtures, as plastic masses or melts. They can also be in the form of their monomers or in the polymerized state in dissolved form as film formers or binders for coating materials or printing inks, for example linseed oil varnish, nitrocellulose, alkyd resins, melamine resins and urea-formaldehyde resins or acrylic resins.

The pigment granules of the invention can be added in any amount effective for colouring to the high molecular mass organic material that is to be pigmented. A pigmented composition judiciously contains 0.1–30% by weight, preferably 1–20% by weight, of pigment granules according to the invention, based on the high molecular mass organic material that is to be pigmented.

For pigmenting organic materials the pigment granules of the invention can be used individually. It is likewise possible, however, in order to obtain different shades or colour effects, to add other colouring constituents, such as white, coloured, black or special-effect pigments, in any desired amounts to the organic substances in addition to the pigment granules of the invention.

The pigmenting of the high molecular mass organic substances with the pigment granules of the invention takes place, for example, by mixing such pigment granules into these substrates using roll mills, mixers or milling apparatus. The pigmented material is subsequently brought into the desired end form by techniques known per se such as calendering, compression moulding, extrusion, spreading, casting or injection moulding. All additives customary in the plastics industry, for example plasticizers, fillers or stabilizers, can be incorporated into the polymers in customary amounts before or after the incorporation of the pigment. In order to produce non-rigid mouldings or to reduce their brittleness it is particularly desirable to incorporate plasticizers, for examples esters of phosphoric, phthalic or sebacic acid, into the high molecular mass compounds before they are shaped.

For pigmenting coating materials and printing inks the high molecular mass organic materials and the pigment granules of the invention, alone or together with customary additives, for example fillers, other pigments, siccatives or plasticizers, are finely dispersed or dissolved in an organic solvent or solvent mixture suitable for all of them. A possible procedure here is to disperse or dissolve the individual components alone, or else two or more of them together, and only then to combine all of the components.

The colourings obtained, for example in plastics, coating materials or printing inks, preferably in coating materials or printing inks and, with particular preference, in coating materials, are notable for excellent properties which are at least equal to those of the powder pigments and in many cases indeed are superior.

Where the high molecular mass material to be pigmented is a coating material, it is in particular a speciality coating material, with very particular preference an automotive coating material.

The examples which follow illustrate the invention (in the examples the parts and percentages are in each case by weight):

EXAMPLE 1

260 kg of 3,6-di-(4'-chlorophenyl)-2,5-dihydropyrrolo[3, 4-c]pyrrole-1,4-dione meeting pigment-grade specification are pasted up homogeneously with 189 kg of deionized water in a conventional annular bed mixer (K-TT™, Drais AG, Mannheim/Germany) to give a formable mass having a solids content of 58%. This moist mass is extruded through a hemispherical shaping section having perforations of 1 mm in diameter in a radial extruder (DG-L1™, Fitzpatrick Co. Europe NV, St.-Niklaas/Belgium) at a conveying speed of 40–50 rpm with a throughput of about 120 kg/h. The cylindrical extrudate particles are then shaped to spheroids in a rounding stage on a granulating plate, and these spheroids are dried in a convection oven at 120° C. to a residual moisture content of <1%. Granules are obtained which are markedly lower in dust than the pigment employed yet while having similar ease of dispersibility. Incorporated by conventional methods in an alkyd/melamine varnish or in flexible PVC, these granules give colourings which are essentially similar to those provided by the pulverulent pigment.

EXAMPLE 2A

The procedure of Example 1 is repeated but using as raw material a mixture, obtainable in analogy to IN-156'867 and U.S. Pat. No. 4,264,552, comprising 90% C.I. Pigment Red 177 [65300] and 10% Staybelite Resin™. 300 parts of this dry mixture are formed into a paste with 200 parts of deionized water (i.e. 74.1% based on the pigment) and 9 parts of trimethylamine in an annular bed mixer, and this paste is extruded to filaments of 0.70 mm in diameter in a radial extruder at a low extrusion pressure. The extruded particles are rounded to give spheroids of about 1 mm which are dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 2B

The procedure of Example 2A is repeated except that filaments of 1.2 mm in diameter are extruded. The extruded particles are rounded to spheroids of about 2 mm. The resulting granules have very good properties.

EXAMPLE 2C

The procedure of Example 2B is repeated except that non-ionic process water (24° dh [German hardness]) is used. The resulting granules have very good properties.

EXAMPLE 3A

The procedure of Example 1 is repeated but using as raw material pure C.I. Pigment Red 220 [20055]. 310 parts of this dry pigment are formed into a paste with 190 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 110° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 3B

The procedure of Example 3A is repeated, except that 190 parts of dry pigment are formed into a paste with 143 parts of a 7% strength solution of Emulan OSN™ (BASF, Leverkusen/Germany) in deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 3C

The procedure of Example 3A is repeated, except that 195 parts of dry pigment are formed into a paste with 14 parts of

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a 7% strength solution of Emulan OSN™ in deionized water and 126 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 4A

The procedure of Example 1 is repeated but using as raw material pure C.I. Pigment Yellow 93 [20710]. 300 parts of this dry pigment are formed into a paste with 200 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion-pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 4B

The procedure of Example 4A is repeated, except that 190 parts of dry pigment are formed into a paste with 143 parts of the 7% strength solution of Emulan OSN™ in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 4C

The procedure of Example 4A is repeated, except that 195 parts of dry pigment are formed into a paste with 14 parts of a 7% strength solution of Emulan OSN™ (BASF, Leverkusen/Germany) in deionized water and 126 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 5A

The procedure of Example 1 is repeated but using as raw material pure C.I. Pigment Orange 64 [12760]. 300 parts of this dry pigment are formed into a paste with 200 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 5B

The procedure of Example 5A is repeated, except that 195 parts of dry pigment are formed into a paste with 71 parts of a 7% strength solution of Emulan OSN™ (BASF, Leverkusen/Germany) in deionized water and 64 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 5C

The procedure of Example 5B is repeated except that, during shaping in the annular bed mixer, 26 parts of a solution consisting of 5 parts of Staybelite Resin™, 6 parts of 25% aqueous ammonia solution and 15 parts of deionized water are added as well. The resulting granules have very good properties.

EXAMPLE 6A

The procedure of Example 1 is repeated but using as raw material pure C.I. Pigment Red 144 [20735]. 260 parts of this dry pigment are formed into a paste with 240 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 6B

The procedure of Example 6A is repeated except that the pigment is used in the form of a water-containing press cake

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comprising 44.7% residual moisture. 372 parts of this moist press cake are formed into a paste with 24 parts of deionized water in an annular bed mixer, and the paste is extruded in a radial extruder at a low extrusion pressure. The resulting granules have very good properties.

EXAMPLE 7A

The procedure of Example 1 is repeated but using as raw material CINQUASIA Magenta B RT-343-D™ (C.I. Pigment Red 202 [73907], Ciba-Geigy AG, Basle/Switzerland). 200 parts of this dry pigment are formed into a paste with 165 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 7B

The procedure of Example 7A is repeated except that 532 parts of dry pigment are formed into a paste with 318 parts of a solution consisting of 29 parts of Staybelite Resin™, 198 parts of 25% strength aqueous ammonia solution and 91 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 7C

The procedure of Example 7B is repeated, except that Staybelite Resin™ is used not in the form of a solution but as a fine powder and is charged directly to the annular bed mixer at the same time as the pigment, the aqueous ammonia solution and the water. The resulting granules have very good properties.

EXAMPLE 8A

The procedure of Example 1 is repeated but using as raw material CINQUASIA Magenta RT-243-D™ (C.I. Pigment Red 202 [73907], Ciba-Geigy AG, Basle/Switzerland). 345 parts of this dry pigment are formed into a paste with 129 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 8B

The procedure of Example 8A is repeated except that 570 parts of dry pigment are formed into a paste with 251 parts of a solution consisting of 30 parts of Staybelite Resin™, 205 parts of 25% strength aqueous ammonia solution and 16 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 8C

The procedure of Example 8A is repeated except that 570 parts of dry pigment are formed into a paste with 205 parts of a solution consisting of 30 parts of Staybelite Resin™, 21 parts of 25% strength aqueous ammonia solution and 154 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 9A

The procedure of Example 1 is repeated but using as raw material CINQUASIA Violet R RT-101-D™ (C.I. Pigment Violet 19 [73900], Ciba-Geigy AG, Basle/Switzerland). 335

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parts of this dry pigment are formed into a paste with 295 parts of deionized water in an annular bed mixer, and this paste is extruded in a radial extruder at low extrusion pressure. The extruded particles are rounded into spheroids and dried in a vacuum oven at 100° C. under reduced pressure. The resulting granules have very good properties.

EXAMPLE 9B

The procedure of Example 9A is repeated except that 594 parts of dry pigment are formed into a paste with 560 parts of a solution consisting of 6 parts of Staybelite Resin™, 41 parts of 25% strength aqueous ammonia solution and 513 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

EXAMPLE 9C

The procedure of Example 9A is repeated except that 594 parts of dry pigment are formed into a paste with 550 parts of a solution consisting of 6 parts of Staybelite Resin™, 3 parts of 25% strength aqueous ammonia solution and 541 parts of deionized water in an annular bed mixer. The resulting granules have very good properties.

What is claimed is:

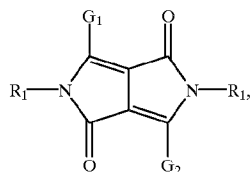
1. Pigment granules with a particle size from 0.5 to 4 mm, which consist of at least 90% by weight of at least one organic pigment selected from the group consisting of diketopyrrolopyrrole, quinacridone, perylene, indanthrone, flavanthrone, isoindolinone and aminoanthraquinone pigments and from 0 to 10% by weight of a binder having from 2 to 7 mol of carboxyl groups per 1000 g and from 0 to 5% by weight of a neutral emulsifier which does not form ions and which dissolves to give a clear solution in water or a C₁-C₄alcohol at a concentration of at least 10 g/100 ml, the binder and the emulsifier together accounting for not more than 10% by weight and all percentages by weight being based on the overall amount of pigment granules, wherein the pigment present in the pigment granules has a particle size of from 0.01 to 10 μm, with the proviso that said granules have a bulk volume not substantially increased by voids left by gas bubbles introduced before granulation and retained in the granules upon drying.

2. Pigment granules according to claim 1, which are essentially spherical.

3. Pigment granules according to claim 1, in which the pigment is a quinacridone pigment.

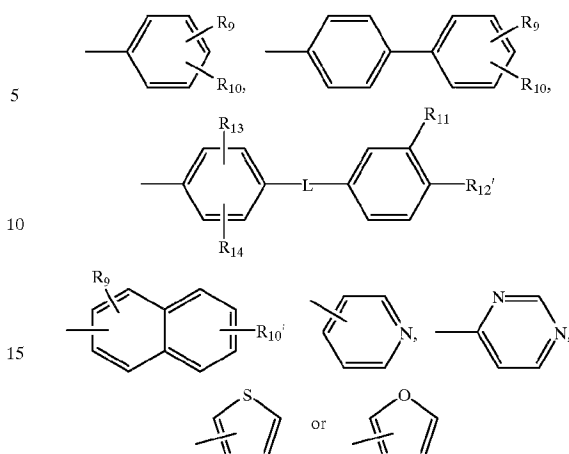
4. Pigment granules according to claim 2, in which the pigment is a diketopyrrolopyrrole.

5. Pigment granules according to claim 4, in which the pigment is a diketopyrrolopyrrole of the formula (VIII)

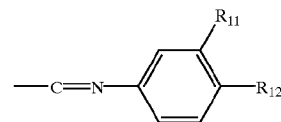


in which R₁ is hydrogen, C₁-C₆alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C₁-C₄alkyl or C₁-C₄alkoxy, and G₁ and G₂ independently of one another are a group of the formula

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in which R₉ and R₁₀ independently of one another are hydrogen, halogen, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₁₈alkylamino, C₂-C₁₈dialkylamino, —CN, —NO₂, phenyl, trifluoromethyl, C₅-C₆cycloalkyl, imidazolyl, pyrazolyl, triazolyl, piperazinyl, pyrrolyl, oxazolyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, morpholinyl, piperidinyl, pyrrolidinyl, —C=N— (C₁-C₁₈alkyl) or



R₁₁ and R₁₂ independently of one another are hydrogen, halogen, C₁-C₆alkyl, C₁-C₆alkoxy or —CN, R₁₃ and R₁₄ independently of one another are hydrogen, halogen, or C₁-C₆alkyl, L is —CH₂—, —CH(CH₃)—, —C(CH₃)₂—, —CH=N—, —N=N—, —O—, —S—, —SO—, —SO₂— or —NR₁₅—, and R₁₅ is hydrogen or C₁-C₆alkyl.

6. Pigment granules according to claim 1, in which the pigment has a mean particle size from 0.2 to 2 μm.

7. Pigment granules according to claim 1, in which the binder contains at least 60% by weight of at least one organic acid.

8. Pigment granules according to claim 7, in which the binder contains at least 5% by weight of abietic acid.

9. Pigment granules according to claim 7, in which the amount of the binder is from 5 to 8% by weight.

10. Pigment granules according to claim 7, in which the amount of the binder is from 0.5 to 2% by weight.

11. Pigment granules with a particle size from 0.5 to 4 mm, which consist of at least 90% by weight of at least one organic pigment selected from the group consisting of diketopyrrolopyrrole, quinacridone, perylene, indanthrone, flavanthrone, isoindolinone and aminoanthraquinone pigments and from 0.5 to 2% by weight of a binder having from 2 to 7 mol of carboxyl groups per 1000 g and from 0 to 5% by weight of a neutral emulsifier which does not form ions and which dissolves to give a clear solution in water or a C₁-C₄alcohol at a concentration of at least 10 g/100 ml, the binder and the emulsifier together accounting for not more than 10% by weight and all percentages by weight being based on the overall amount of pigment granules, wherein the pigment present in the pigment granules has a particle size of from 0.01 to 10 μm.

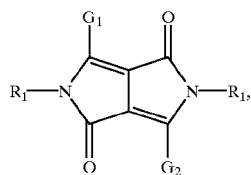
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12. Pigment granules according to claim 11, which are essentially spherical.

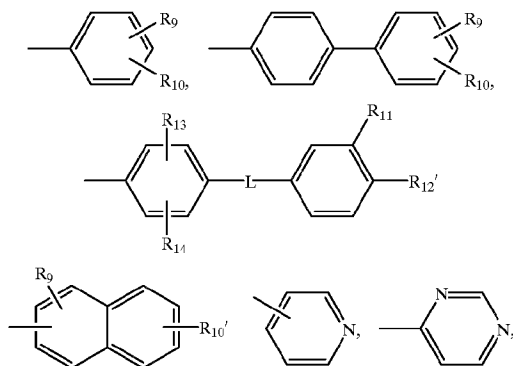
13. Pigment granules according to claim 11, in which the pigment is a quinacridone pigment.

14. Pigment granules according to claim 11, in which the pigment is a diketopyrrolopyrrole pigment.

15. Pigment granules according to claim 14, in which the pigment is a diketopyrrolopyrrole of the formula (VIII)

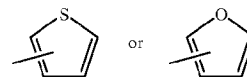


in which R₁ is hydrogen, C₁-C₆alkyl, phenyl or benzyl or is phenethyl which is unsubstituted or substituted by halogen, C₁-C₄alkyl or C₁-C₄alkoxy, and G₁ and G₂ independently of one another are a group of the formula

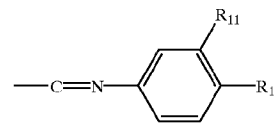


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in which R₉ and R₁₀ independently of one another are hydrogen, halogen, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₁₈alkylamino, C₂-C₁₈dialkylamino, —CN, —NO₂, phenyl, trifluoromethyl, C₅-C₆cycloalkyl, imidazolyl, pyrazolyl, triazolyl, piperazinyl, pyrrolyl, oxazolyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, morpholinyl, piperidinyl, pyrrolidinyl, —C=N— (C₁-C₁₈alkyl) or



R₁₁ and R₁₂ independently of one another are hydrogen, halogen, C₁-C₆alkyl, C₁-C₆alkoxy or —CN, R₁₃ and R₁₄ independently of one another are hydrogen, halogen or C₁-C₆alkyl, L is —CH₂—, —CH(CH₃)—, —C(CH₃)₂—, —CH=N—, —N=N—, —O—, —S—, —SO—, —SO₂— or —NR₁₅—, and R₁₅ is hydrogen or C₁-C₆alkyl.

16. Pigment granules according to claim 11, in which the pigment has a mean particle size from 0.2 to 2 μm.

17. Pigment granules according to claim 11, in which the binder contains at least 60% by weight of at least one organic acid.

18. Pigment granules according to claim 17, in which the binder contains at least 5% by weight of abietic acid.

* * * * *

EXHIBIT C



US006908675B1

(12) **United States Patent**
Bohach et al.

(10) **Patent No.:** **US 6,908,675 B1**
(45) **Date of Patent:** **Jun. 21, 2005**

(54) **PROCESS TO REDUCE DUSTING AND
IMPROVE FLOW PROPERTIES OF
PIGMENTS AND POWDERS**

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/407,334**

(22) Filed: **Apr. 7, 2003**

Related U.S. Application Data

(60) Provisional application No. 60/375,115, filed on Apr. 22,
2002.

(51) **Int. Cl.**⁷ **B32B 5/16**

(52) **U.S. Cl.** **428/402**; 428/403; 428/404;
428/407; 106/436; 427/212

(58) **Field of Search** 428/402, 403,
428/404, 407; 106/436; 427/212

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Primary Examiner—Leszek B Kiliman

(57) **ABSTRACT**

Titanium Dioxide and other pigments or powders processed by this present process are smoothly discharging, low dusting, agglomerated, compaction resistant, extremely friable and fully dispersable. The process for the production of smoothly discharging pigment or powder consists of gently blending in the presence of an air flow and an electrostatic charge where said pigment or powder is being agglomerated with or without a treated or non-treated seed particle of the same or similar pigment whereas said pigment or powder in accordance with the invention yields a composition of a substantially spherical particulate that has a pseudo-particle size of 0.1–5.0 mm in the form of smoothly discharging, low dusting, non-sticky, agglomerated, compaction resistant pigment or powder, in which said pigment or powder particles are 80%–99.9% by weight, pigment, and in which the pigments or powders are compatible with inks, paints and plastics, and can be readily dispersed and incorporated into the same.

20 Claims, No Drawings

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PROCESS TO REDUCE DUSTING AND IMPROVE FLOW PROPERTIES OF PIGMENTS AND POWDERS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of the provisional application U.S. Ser. No. 60/375,115 filed 22 Apr. 2002.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable

REFERENCE TO A MICROFICHE APPENDIX

Not applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for manufacturing low-dusting, smoothly-discharging, easily dispersible titanium dioxide and other pigments and cohesive powders that resist compaction, aging, lumping and caking, in which the pigment or powder has been subjected to micronizing or jet milling, sand milling, hammer milling, ground up or the like for use in foodstuffs, cosmetics, detergents, paint and plastics, inks and elastomers.

2. Description of the Prior Art

Titanium dioxide, iron oxides pigments, pearlescent pigments and powders including talc, and other metal oxide pigments, are used in the cosmetics, detergents paint, plastics, construction and other industries where pigments or powders are added to color and /or opacify the desired application and usually through intensive mixing. Some essential performance properties for the pigments are the dispersability of the pigment throughout the application system, the ease of handling and metering and dusting.

Dispersability is a measure of the ease with which the powder or pigment particles can be uniformly and intimately mixed in a system. Poor dispersion of particles can cause large agglomerates that may result in lumps, surface imperfections, color streaks, non-uniform coloration, or incomplete color development within the product. A further problem exists for pelletized or granular powder or pigment in that the amount of energy expended to disperse those types is exceptionally high and time consuming.

Inorganic pigments are normally produced for and used in the paints, plastics, or elastomer industries, and are in the form of a finely divided powder. The powders are usually jet-milled, sand milled, hammer milled or roller milled as a finishing step in their production. Milling contributes to dispersability and gloss, but milled pigments exhibit poor dry flow characteristics and are dusty. Such pigments all have the great disadvantage of producing dust. During their use, costly measures (for example of a workplace safety, ecological or quality assurance nature) are necessary, and valuable material is lost.

The ease of handling or lack thereof, takes into consideration difficulties associated with storing, transportation and mixing of the pigments in the manufacturing and processing system. The stability of pigment granules is necessary for good storage and transporting, thus averting aging, or the clumping of pigment into large agglomerates when in storage subjected to heat, humidity and pressure. This stability is brought about by using the high cohesive

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forces within the individual particle to an advantage rather than a disadvantage and depends on the compaction pressure or forming method used in making the granules. It should be noted that the goals of achieving good dispersability and good stability are usually contrary to one another.

Problems repeatedly experienced in handling large quantities of powders are caking, rat holing, bridging, or aging in compressed storage and clogging with a loss of pigment flow when in feed bins. Combined with the problems associated with dust from finely divided powders it is frequently the case that pigment compositions are preferred in pellet particle or granular form.

Surface treatment of pigments to achieve improved performance characteristics such as dispersion in coatings and plastic compositions, and may help in dry flow, is known in the art as is shown in the following patents:
U.S. Pat. No. 3,925,095 teaches that treating of inorganic pigments or fillers with hydroxyalkylated alkylene diamine dispersing agent will help flowability and dispersability in many applications.

U.S. Pat. No. 4,127,421 discloses the aqueous treatment of a lead chromate-containing pigment with a friable hydrocarbon resin and a cationic surfactant will produce free flowing, non-dusting granules.

Also known in the art is the absorption of waxes, aqueous solutions, polymers, and other oils, fats, or surfactants to help form free flowing granules.

In U.S. Pat. No. 4,285,994 the invention comprises a free-flowing nucleated pigment 50% by weight or more, in a spherical particulate of spray-chilled wax composition that has a coating and is partially absorbed into a pigment.

In U.S. Pat. No. 4,056,402, shows that aqueous slurries of inorganic or organic pigments are milled in the presence of a nonionic, polyether alcohol dispersing agent and nonionic cellulose ether to reduce dusting and improve dispersability. U.S. Pat. No. 4,310,483 demonstrates a process for producing a granulate of fusible additives and pigments for plastics by thermal tumbling granulation, that comprises mixing the additive in powder form with an additive that softens between 30 degree C. and 200 degree C. and which have a particle size of 0.1–2.0 mm.

U.S. Pat. No. 4,375,520. This patent teaches the production of dustless particles, including pigments, by treatment of the particles with a solid low-molecular weight polymer and a liquid polymer substance such as expoxidized soybean oil at temperatures above the melting point of the polymer.

U.S. Pat. No. 4,464,203 discloses the treatment of inorganic or organic pigments with an amine and ethylene oxide block copolymer surfactant to improve pigment dispersibility and other properties in many applications

U.S. Pat. No. 4,762,523 discloses coating a moist pigment with a polyester surfactant, then adding mineral oil or wax to the pigment and applying high shear stresses to achieve a free-flowing, permanently non-dusting pigment.

U.S. Pat. No. 5,604,279 shows that a colorant composition comprising at least one colorant very finely dispersed in a base material which is solid at room temperature is suitable for producing master batches and provides the way to dust-free colorant compositions

One method for making free-flowing powders with low dust can be obtained by spray drying. These products generally exhibit poor pigmentary properties. Thus, pigment end users have generally had to choose between free-flowing, low dusting, spray-dried pigments with poor pigmentary properties and dusty, milled pigments with poor flow characteristics.

U.S. Pat. No. 3,660,129 establishes that titanium dioxide pigments are coated with hydrous oxides, then sand-milled and spray-dried to improve flowability.

U.S. Pat. Nos. (4,810,305) and (5,035,748) represent spray pelletization using siloxanes as hydrophobic additives. The stated spray dryer generally results in small particle sizes with a high proportion of fines. This means that a substantial proportion of the material is not realized from the dryer as directly usable pellets, but as fines, which must first be retained in a filter and then returned to the process. In spray dried products, hydrophobic post-treatment results in particles that have somewhat good flow properties but produce exceptionally large quantities of dust.

U.S. Pat. No. 5,199,986 demonstrates that colored building materials are produced by incorporating into the building materials inorganic pigments in the form of granulates which are free-flowing and not dust forming where the pigments are produced from spray dried granulates by post-granulating

U.S. Pat. No. 5,199,986 also discloses a process wherein previously spray-dried inorganic pigment granules are coated with water and solutions of salts of boron, aluminum, silicon, titanium, zinc, brass, or tin, to improve processing and reduce dust production.

U.S. Pat. Nos. 5,733,365 and 5,908,498 illustrate a process for manufacturing titanium dioxide characterized by improved flowability, low dust production, and good dispersibility, without the energy-intensive and expensive step of micronization. In this process, at least one treating agent is deposited on a pigment that has been sand milled, as an aqueous slurry. The treated slurry is then spray dried for end-use performance without jet milling or micronization.

Known production processes for pigment pellets in addition to the spray granulation (spray drying using a disk or jet) are agglomeration pelletization (mixers, fluidized bed pelletizers, plates or pins) or compaction processes.

U.S. Pat. No. 6,132,505 instructs that inorganic pigment pellets comprising the steps of mixing at least one inorganic pigment powder with at least one water-soluble, hydrophilic or hydrophobic/hydrophilic auxiliary substance liquid in a quantity of 0.1 to 10 wt. %, relative to the pigment powder, and pelletizing the resultant mixture of by compacting and crushing the resultant mixture, one fraction having an average particle size of 100 to 1000 μm .

None of the aforementioned patents enlighten, teach or even suggest about a process consisting of mixing of pigments with the presence an air flow and an electrostatic charge to obtain a pseudo particle to provide an extremely friable, highly dispersible pigment that is smoothly discharging, with reduced dusting, resistant to compaction and easily metered, and this is the subject of this application.

DISCLOSURE OF THE INVENTION

The present invention implements the process for the continuous production of smoothly discharging, easily metered low dusting pigment compositions with good dispersibility even after long term compacted storage or aging—an effect of the environment and especially occurs as TiO_2 pigment is exposed to high humidity and high temperature. As a result, said TiO_2 tends to agglomerate into large lumps and there can be loss of optical properties of said titanium pigment when incorporated into powder coatings and plastics applications. This present process is comprised of blending or mixing a powdered pigment with or without a seed pigment for a time sufficient in the presence of airflow and an electrostatic charges and utilizing Van der Waal forces for substantially all of the pigment to be agglomerated into extremely friable spherical ersatz particles and is utilized to overcome aging as well. Temperatures used range from ambient to 100 deg C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is an objective of this invention to produce free flowing, low dust pigment compositions, which can be dust free. It is also an objective of this invention for the pigment to have smooth flow and handling characteristics, resulting in little to no caking or compaction during storage and is easily dispersed after being stored in a compressed state. These pseudo-particles can be used for coloring paint, inks, plastics, elastomers, cosmetics or ceramics and other powder materials. These low-dust, smoothly flow compositions are particularly suitable for use with metering and feeding devices

The invention is particularly effective with inorganic oxide pigments such as alumina, magnesia, titanium dioxide and zirconia. The invention can be practiced on materials less than about one micron in average diameter, and is preferably practiced on pigments and fillers, having average particle sizes of about 0.01 to about 10 microns. The spherical agglomerates produced are preferably at least about 0.01 millimeters in diameter, most preferably from about 0.1 millimeters to about 4 millimeters in diameter.

The pigments that can undergo the described process to provide the improved pigments of the present invention include any of the white or colored, opacifying or non-opacifying particulate pigments (or mineral pigments) known and employed in the surface coatings (e.g., paint) and plastics industries. For purposes of this present detailed description, the term pigments is used broadly to describe materials which are particulate by nature and nonvolatile in use and typically are most usually referred to as inerts, fillers, extenders, reinforcing pigments and the like and are preferably inorganic pigments.

Representative examples of pigments that can be treated are defined to provide the improved pigments of this invention include white opacifying pigments such as titanium dioxide, basic carbonate white lead, basic sulfate white lead, basic silicate white lead, zinc sulfide, zinc oxide, composite pigments of zinc sulfide and barium sulfate, antimony oxide and the like, white extender pigments such as calcium carbonate, calcium sulfate, china and kaolin clays, mica, diatomaceous earth and colored pigments such as iron oxide, lead oxide, cadmium sulfide, cadmium selenide, lead chromate, zinc chromate, nickel titanate, chromium oxide, and the like. Of all the pigments useful in producing the improved pigments of the present invention, the most preferred pigment is titanium dioxide.

Titanium dioxide pigment for use in the process of this invention can be either the anatase or rutile crystalline structure or a combination thereof. The pigment may be produced by known commercial processes which are familiar to those of skill in this art but which those processes do not form any part of the present invention. The specific pigment can be produced by either the well-known sulfate process or the well-known vapor phase oxidation of titanium tetrachloride process.

The titanium dioxide particles are particularly useful in the present invention that include anatase and rutile crystalline forms and may be treated or coated, e.g., with one or more oxides or hydroxides of metals including aluminum, antimony, beryllium, cerium, hafnium, lead, magnesium, niobium, silicon, tantalum, titanium, tin, zinc, or zirconium. The pigments of titania or other inorganic oxides can contain aluminum, introduced by any suitable method, including the co-oxidation of halides of titanium, (or other metal) and aluminum as in the "chloride process" or the addition of

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aluminum compounds prior to calcination in the "sulphate process". Other products, but not all inclusive, that can be manufactured as specified in this invention, to improve the properties include fly ash, powdered foodstuffs, cement, cosmetics, polytetrafluoroethylene, powders, talc and clay.

According to one aspect of the present invention, a smoothly discharging pigment consists of spherical faux particles, the pigment is 91% by weight or more pigment and may be to the extent of 99.9% by weight. Also present, but not significantly, are one or more surface treatments that are standard on some pigments.

In another aspect, minute amounts of environmentally friendly and non-toxic polyols, glycols and/or glycol ethers and/or siloxanes may be used as part of the process, where the pseudo-particles are not hindered in water dispersion, but actually aided. These agents are in minute amounts that they will not affect paint, ink or concrete processing and some will not affect polymer processing such as blown or cast film with lacing or the like. These pseudo-particles can be used for the pigmentation of aqueous or non-aqueous systems requiring low dust, good material flow, and accurate metering or feeding properties.

EXAMPLE 1

100 parts by weight of finely ground, black iron oxide pigment is mixed with the seed pigment of the same with 0.5 to 1.5 parts by total weight of propylene glycol. The mixture is placed in a specialized mixing vessel and blended. The process is continued and within about 0.10–15 minutes complete pseudo-particle formation occurs, and a smoothly discharging product is obtained.

Increase in bulk density of the processed pigment is nominally 36%

Angle of repose decreased from 55.6 deg to 41.6 deg, a decrease of 25%.

Increase in flow rate of the processed powder was from 100 gms. in 129 seconds to 100 gms. in 20 seconds.

48-hour compression test of between 4 and 6 psi yielded a completely crumbled pigment discharge upon ejection from the forming cylinder. The unprocessed pigment was a hard singular mass that did not even fracture upon ejection.

Decrease in available dust nominally 60%.

EXAMPLE 2

100 parts by weight of finely ground, black iron oxide pigment is mixed with the seed pigment of the same with 0.5 to 1 parts by total weight of polydimethylsiloxane, 320 cs. The mixture is blended in a mixing vessel of specialized design. The process is continued and within about 0.25–15 minutes, pseudo particle formation is complete, and a smoothly discharging product is obtained.

Increase in bulk density of the processed pigment is nominally 29%

Angle of repose decreased from 55.6 deg to 38 deg, a decrease of 32%.

Increase in flow rate of the processed powder was from 100 gms in 129 seconds to 100 gms. in 20 seconds.

48-hour compression test of between 4 and 6 psi yielded a completely crumbled, pigment discharge upon ejection from the forming cylinder. The unprocessed pigment was a hard singular mass that did not even fracture upon ejection.

Decrease in available dust nominally 55%.

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EXAMPLE 3

100 parts by weight of a universal grade rutile titanium dioxide is blended, at temperature, in a mixing vessel of special design. The process is continued and within about 0.25–15 minutes pseudo particle formation is complete, and a smoothly discharging product is obtained.

Increase in bulk density of the processed pigment is nominally 15%

Angle of repose decreased from 52. deg to 38.6 deg, a decrease of ~26%.

Increase in flow rate of the processed pigment was from 50 gms at 1.6 gm/sec seconds to 50 gms at 6.2 gm/sec seconds.

48-hour compression test of between 4 and 5 psi yielded a completely crumbled, pigment discharge upon ejection from the forming cylinder. The unprocessed pigment was a hard singular mass that did not even fracture upon ejection.

Decrease in available dust nominally 70%.

Paint Dispersion comparisons on the Hegman scale are consistent with the unprocessed code standard pigment

EXAMPLE 4

100 parts by weight of a hydrophobic plastics grade rutile titanium dioxide, at temperature, is blended in a specialized mixing vessel. The process is continued and within about 0.1–15 minutes pseudo particle formation is complete, and a smoothly discharging product is obtained

Increase in bulk density of the processed pigment is nominally 16%

Angle of repose decreased from 50.5 deg to 38.3 deg, a decrease of ~27%.

Increase in flow rate of the processed pigment was from 50 gms at 1.9 gm/sec to 50 gms. at 8.3 gm/sec seconds.

48-hour compression test of between 4 and 5 psi yielded a completely crumbled, pigment discharge upon ejection from the forming cylinder. The unprocessed pigment was a hard singular mass that did not fracture upon ejection.

Decrease in available dust nominally 80%.

Dispersion comparisons through a Brabender Extruder and into this polymer film are consistent with the unprocessed code standard pigment.

In all cases, dust values are assessed as a weight in comparison with the powder. The subjective visual observation of dust on transfer between containers is also used by way of comparison. In all cases, flow is determined by measuring the drain time in seconds from a cylindrical vessel (volume 50 or 100 gm) with a 60 deg. conical base through a defined bore (generally 10 mm).

What is claimed is:

1. A process for the production of a free-flowing powders selected from the group comprising titanium dioxide pigments iron oxide pigments, basic carbonate white lead, basic sulfate white lead, basic silicate white lead, zinc sulfide, zinc oxide, composite pigments of zinc sulfide and barium sulfate, antimony oxide and the like, white extender pigments such as calcium carbonate, calcium sulfate, china and kaolin clays, mica, diatomaceous earth and colored pigments such as iron oxide, lead oxide, cadmium sulfide, cadmium selenide, lead chromate, zinc chromate, nickel titanate, chromium oxide, alumina, magnesia, zirconia, kaolin clays, and polytetrafluoroethylene powders and the mixtures thereof which adhere intimately together to form substantially

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spherical pseudo-particles ranging in size from 0.2 mm up to 5.0 mm in diameter where by the pigment is blended in a specially designed mixing vessel with the presence of an electrostatic charge and a air flow and reduces the dustiness of the powders at by a minimum of 50 percent.

2. The process according to claim 1 wherein intimate blending and mixing is carried out at a temperature falling within the range from 12 deg C. to 100 deg C.

3. The process of claim 1 wherein nucleation and layering is carried out for a time of from about 0.25 minutes to about 15 minutes.

4. The Process according to claim 1, which includes the step of post treating of said pigments, and powders and mixtures thereof.

5. The Process according to claim 1, wherein the post treating step comprises application of alcohols, esters, silicone compounds, glycols, polyols, or polyethers, in a quantity of 0.01 to 3 wt. %, relative to pigment pellets.

6. A low-dusting, free-flowing, titanium dioxide pigments, iron oxide pigments, chromium oxide pigments, mixed metal oxide pigments, kaolin clays, and polytetrafluorethylene powders produced by the process of claim 1.

7. The spherical agglomerates produced by the process of claim 1 wherein pigment is titanium dioxide pigment.

8. The spherical agglomerates produced by the process of claim 1 wherein pigments and powders are comprised of material selected from the group comprising iron oxide pigments, chromium oxide pigments, mixed metal oxide pigments, metal oxide pigments, kaolin clays, and polytetrafluorethylene powders and mixtures thereof.

9. The process of claim 1 wherein a metal oxide coating on the pigment is present in an amount of from about 0 percent to about 1.5 percent by weight.

10. The spherical agglomerates produced by the process of claim 1 wherein titanium dioxide or iron oxide pigments, chromium oxide pigments, mixed metal oxide pigments, metal oxide pigments, kaolin clays, or polytetrafluorethylene powders is coated with at least one metal oxide and contains an oxide or hydroxide of aluminum, silicon or zirconium.

11. A specially designed mixer for processing as claimed in claim 1 is used to carry said titanium dioxide or iron oxide pigments, chromium oxide pigments, mixed metal oxide

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pigments, metal oxide pigments, kaolin clays, or polytetrafluorethylene powders to continuously produce free flowing particles while transporting the beyond the pigments apparent angle of repose.

12. The process mixing vessel of claim 1 is electrically grounded to prevent electrostatic discharge.

13. The process of claim 1 wherein electrostatic charges, van der Waal forces, in addition to any inherent electrostatic charges, cause self-attraction whereby nucleation takes effect.

14. The process of claim 1 wherein continuous mixing, lifting and rolling and avalanching provides a free flowing titanium dioxide or iron oxide pigments, chromium oxide pigments, mixed metal oxide pigments, metal oxide pigments, kaolin clays, or polytetrafluorethylene powders utilizes and promulgates a static charge to cause attraction of particles to one another reducing dust and nucleates faux particles to give a random size.

15. The process of claim 1 wherein vibration at various locations on the unit, will deareate the titanium dioxide or iron oxide pigments, chromium oxide pigments, mixed metal oxide pigments, metal oxide pigments, kaolin clays, or polytetrafluorethylene powders to increase the bulk density of the material but not to cause densification and caking of the material to prohibit dispersion.

16. The process of claim 1 wherein vibratory effects applied in the process on the inlet and on the shell of the mixer between the ranges of 1 and 3600 Hz induce deaerating of the pigment and aiding increasing bulk density.

17. The process of claim 1 wherein airflow through the unit is substantially enough to help dissipate heat from any hot material, aids in the nucleation and yet is not forceful enough to carry over any measurable quantity of pigment or powder.

18. A low-dusting, free-flowing, micronized or non-micronized pigment or powder produced by the process of claim 1.

19. A paint formulation containing the pigment or powder of claim 18.

20. A plastic formulation or masterbatch containing the pigment or powder of claim 18.

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RELATED PROCEEDINGS APPENDIX

There are no copies of decisions rendered by a Court or the Board regarding any related appeals or interferences, because there are no related appeals or interferences.